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Tracing the Input and Evolution of Municipal Water in Springs and Tributaries of the Bull Creek Watershed, Austin, TX

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Tracing the Input and Evolution of Municipal Water in Springs and Tributaries of the Bull Creek Watershed, Austin, TX

by

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Abstract

Tracing the Input and Evolution of Municipal Water in Springs and Tributaries of the Bull Creek Watershed, Austin, TX

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The conservation of freshwater resources is fundamental in supporting modern society and preserving natural habitats and ecosystems. Deterioration of water quality in urban landscapes and loss of municipal water to leaky water distribution infrastructure are two substantial challenges to water-resource sustainability. I examine the geochemistry of streamwater, municipal water, wastewater, soil, and bedrock from the Bull Creek watershed, a rapidly urbanizing watershed in Austin, Texas, to achieve a better understanding of the processes of geochemical evolution as anthropogenically-sourced water recharges natural systems. Urbanization patterns in the Bull Creek watershed have created a contiguous expanse of urban development that covers roughly two thirds of the watershed, whereas the remaining third is rural, enabling direct comparison between urban and rural streamwater from a single watershed. Results indicate that Na, Cl, K, and SO_4 in urban springs and tributaries are elevated more than two-fold in comparison with rural springs and tributaries. A comparison of Sr concentration and Sr isotopic composition for spring and tributary samples indicates that

municipal water and wastewater provide a substantial contribution to the urbanized stream branches of Bull Creek. This water is reactive in the subsurface after it leaks from the municipal system, evolving via a pathway of water-rock interaction with limestone.

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Chapter 1: Introduction

Water scarcity is an issue that is common to many regions around the world. In central Texas, persistent drought beginning in 2011 reduced the storage of the water-supply reservoir system that provides municipal water to the city of Austin (CoA) to the second lowest recorded volume in its history, resulting in the enforcement of mandatory water-use restrictions. These restrictions have not been lifted as of August 15, 2014 as storage in the reservoirs has not risen above 50% since August, 2011 (Lower Colorado River Authority, 2014). Water scarcity across Texas will likely be exacerbated in the 21st century as the state is expecting rapid population growth (United States Census, 2013) and the availability of freshwater resources is projected to decline in the coming decades (Banner et al., 2010), prompting legislators and voters to pass a proposition that sets aside two billion dollars from the Texas Economic Stabilization fund (colloquially known as the Rainy Day Fund) to start a low-interest loan program for water development (Texas State Legislature, 2013).

This study attends to two primary water issues in Central Texas – a decrease in municipal water quantity resulting from leaky pipe infrastructure and a decrease in quality resulting from urban stream adulteration – by examining dissolved streamwater constituents and land use within the Bull Creek watershed in Austin, Texas (Fig. 1, Fig. 2). Covering an area of 63 square kilometers, the Bull Creek watershed is the largest single watershed that drains into Lake Austin, a manmade lake along the Colorado River that is the primary reservoir for Austin municipal water. During periods when dam releases to Lake Austin from upstream reservoirs are curtailed, Bull Creek can provide up to 37% of Lake Austin inflow on a monthly basis (Geismar, 2001). The northern reaches of the watershed lie within the recharge zone for the northern segment of the Edwards aquifer (Fig. 1), which provides water for other rapidly growing municipalities in central Texas (i.e. Georgetown, Pflugerville, and Round Rock). Due to its contribution to the northern segment, contamination in Bull Creek can serve as a proxy for the effects of urbanization in the regional Edwards aquifer, the primary source of water-supply for millions of people in New Braunfels, San Marcos, and San Antonio (Fig. 1; Sharp and Banner, 1997).

Along with preservation of water quality for anthropogenic use, the conservation of natural stream environments in the Bull Creek watershed is imperative for ecological concerns. The watershed is home to the Jollyville Plateau salamander (*Eurycea tonkawae*) and is a nesting site for migratory passerines like the golden-cheeked warbler *(Setophaga chrysoparia*) and the black-capped vireo (*Vireo atricapilla*), all identified as threatened species under the U.S. Endangered Species Act of 1973. Recognizing the need for endangered-species protection, local governments implemented the Balcones Canyonlands Conservation Plan (BCCP) in 1996. Under the BCCP, the City of Austin acquired a contiguous tract of 4.6 square kilometers in the Bull Creek watershed for the protection of black-capped vireo nesting habitat. This also provides habitat for the Jollyville Plateau salamander, though both species are subject to urban contaminants in the streams that border the preserve. A three-fold reduction in population size has been noted when comparing Jollyville Plateau salamander communities in urban versus rural streams (Bowles et al., 2006). Additionally, a connection between thyroidal impairment of Eurasian dipper (*Cinclus Cinclus*) nestlings and urban-stream contaminants has been demonstrated in Wales, United Kingdom (Morrisey et al., 2014). This study provides an example of a disruption in avian development specific to birds that nest in the vicinity of urban streamwater such as the golden cheeked warbler and the black-capped vireo.

It is well established that urban development has the potential to impose a variety of disturbances on local stream ecosystems, including degradation and loss of habitat, elevated concentrations of contaminants and nutrients, and a reduced storm water retention period (Klein, 1979; Paul and Meyer, 2001; Rose and Peters, 2001; Walsh et al., 2005). As a measure of water degradation, the dissolved ions in streamwater are subject to rainwater dilution, evaporation, mixing of different water bodies, oxidation, rock dissolution, and ion exchange with clay and soil units, which have the potential to modify ion concentrations. Ratios of naturally occurring isotopes, which respond differently to these processes, can be used in conjunction with ion concentrations to provide insight into streamwater evolution (Hosono et al., 2009, 2010 & 2011; Li et al., 2010; Christian et al., 2011). Here I apply the strontium (Sr) isotope ratio ($^{87}Sr/^{86}Sr$) because the various sources of Sr in the Austin area provide traceable endmembers with respect to $^{87}Sr/^{86}Sr$.

As a result of land development, some of the watersheds in Austin are highly urbanized, while others remain in a rural, relatively undeveloped state (Fig. 2). A previous study in Austin demonstrated that stream-water $^{87}Sr/^{86}Sr$ values correlate with elevated levels of dissolved anthropogenic ions (e.g. F, Cl) when comparing mean watershed stream-water values for eight different watersheds (Christian et al., 2011). Mean $^{87}Sr/^{86}Sr$ values also correlates with physical indicators of urbanization (e.g. percent impervious cover, population density) for the eight watersheds (Christian et al., 2011). Streams in watersheds that are heavily urbanized have higher mean $^{87}Sr/^{86}Sr$ values ($^{87}Sr/^{86}Sr = 0.7088$) than streams in rural watersheds ($^{87}Sr/^{86}Sr = 0.7079$; Christian et al., 2011). In the Austin area, where groundwater ($^{87}Sr/^{86}Sr = 0.7076$, reflective of local Cretaceous limestone) and municipal water ($^{87}Sr/^{86}Sr = 0.7090$) have contrasting $^{87}Sr/^{86}Sr$ values, the contribution of municipal water and wastewater to surface water is inferred from the high $^{87}Sr/^{86}Sr$ value found in urbanized streams (Christian et al., 2011). This finding is significant because it indicates that leaky underground infrastructure may be a substantial contributor of water to urban streams. In this thesis, I refer to City of Austin supply water (tap, irrigation, and industrial supply) as municipal water, and the combination of municipal and wastewater are herein referred to as anthropogenic water.

In the year 2000, the City of Austin distributed an average of 541 million liters of municipal water per day, yet it treated a daily average of 318 million liters per day at its wastewater facilities. This loss of 223 million liters per day adds up to 81 billion liters removed from the municipal system each year. While more than half of this water is assumed to be used for irrigation, this figure represents the volume of treated water available as urban runoff/recharge (Garcia-Fresca & Sharp, 2005). By comparing the volume of water delivered to the volume of water billed, the city estimates that 5.7% of treated municipal water was lost to leaky municipal and wastewater pipes in 2009 (Garcia-Fresca & Sharp, 2005). During 2011 and 2012, the City of Austin lost an estimated combined 26 billion liters of water, roughly the entire volume of Lake Austin, to leaky or broken pipes (Texas Water Development Board, 2001; Pierotti, 2013).

By focusing on the Bull Creek watershed, I minimize geologic heterogeneity while maintaining the pronounced gradient in urbanization that allows for direct comparison between rural and urban streams, in order to test the citywide hypotheses developed by Christian et al. (2011). Bull Creek provides a distinctively well-constrained setting for scaling down the Austin-area urbanization study to a single watershed. Some Bull Creek tributaries are sourced in fully-urbanized reaches of the watershed, whereas others flow in an exclusively rural setting (Fig. 3; Fig. 4). Much like the eight watersheds examined by Christian et al. (2011), the land development history within the Bull Creek watershed has created a distinct contrast with respect to urbanization. In this study, I sampled individual springs and tributaries from the Bull Creek watershed, and classify each site as either rural or urban based upon the land use in the respective up-gradient sub-watershed.

Our geochemical characterization of the tributaries and springs in the Bull Creek watershed provides unique insight into the effects of urbanization on streamwater quality within a single watershed by comparing streamwater with a range of potential sources of dissolved ions (herein referred to as endmembers). I compare the composition of Bull Creek streamwater samples to bedrock, soil, and municipal water endmembers collected from within the watershed (Fig. 3), as well as wastewater endmembers from the greater Austin area (City of Austin, 2012), to resolve the influence of urbanization on streamwater quality. A principal finding from this study is that urbanization is a primary modifier of streamwater chemistry in the Bull Creek watershed, and that anthropogenic water influx is key part of this modification providing an estimated 50-90% contribution to baseflow. Furthermore, two novel conclusions that follow on from this finding are that 1) this leaked anthropogenic water is subject to water/rock interaction that alters its composition as groundwater, and 2) discrete streamwater sites reveal substantially different levels of influence from anthropogenic water influx, even within several hundred meters of each other.

Chapter 2: Setting

The Bull Creek watershed is located west of the regionally-extensive Balcones Fault Zone in Austin, Texas. Here, normal faulting that occurred during the Miocene, related to the subsidence of the Texas Coastal Plain, has exposed Cretaceous-age rocks along the Edwards Plateau (Grimshaw and Woodruff, 1986). Austin sprawls on both sides of this fault zone, situated in the transition zone between the Blackland Prairie to the southeast and the Edwards Plateau to the northwest. The watershed dissects the Edwards Plateau and drains to the south into the Colorado River, dropping about 200 meters from its highest point to the creek mouth at Lake Austin. The main channel of Bull Creek is approximately 21 kilometers long, with a grade of about 5 meters per kilometer (Ging, 1995). The region is characterized by rolling slopes with steep canyons leading to valleys about 100 meters deep (Marquez, 1947).

2.1 Geology, Soils, and Hydrogeology

The stratigraphy of the Bull Creek watershed is described by Marquez (1947) and Cox (1934), and is summarized below. The Bull Creek watershed is underlain by (from oldest to youngest) the Glen Rose formation, the Walnut formation, the Comanche Peak formation, and the Edwards formation, all of which are limestone units that formed in the shallow Fredericksburg sea during the Cretaceous Period (Fig. 5). A setting of reefs and lagoons, characterized by recurring periods of restricted flow alternating with an open marine environment is the inferred depositional setting as the evaporate minerals dolomite and gypsum are commonly found in the Edwards formation and Glen Rose formation, where mud cracks are also observed.

The Glen Rose formation ranges from chalky, calcareous limestone in the lower portion to alternating beds of clayey marl and limestone in the upper regions. The Walnut formation is characterized by beds of yellow clay and shale that alternate with layers of white limestone, banded with nodular and shell agglomerate layers. The Comanche Peak formation is a relatively thin transitional bed between the Edwards formation and the Walnut formation that resembles Edwards limestone. The Edwards formation is coarse-grained, relatively durable limestone that acts as a cap rock for hills within the watershed. Eroded clay and shale from the Walnut formation and upper Glen Rose formation covers the steep slopes around the hills (Marquez, 1947).

The dominant soil types in the Bull Creek watershed are Speck and San Saba clay, Tarrant, Brackett, and Volente (Fig. 6). Soil types are described in Werchan et al., (1974) and are summarized here. Speck and San Saba clays are classified as Redland range soils (Snatic, 2013) and cover only 2% of the watershed. Maximum thickness for these soil groups is around 35 cm. Tarrant soils are characterized by a stony, clayey layer ranging from 10-35 cm thick. Brackett soils have a maximum thickness of 35 cm, and are similar to Tarrant composition with the notable presence of loam, silt, and gravel. Both Tarrant and Brackett overlay hill tops and hillsides for a combined 89% coverage of the watershed. The Volente complex accumulates in valleys at the foot of the Tarrant and Brackett exposures, ranging in thickness from 85-125 cm. The respective thickness for each layer is provided by a survey of the soils in Travis County (Austin is located in Travis County). In general, the exposures of Speck and San Saba clay, Brackett, and Tarrant, which cover the uplifted Edwards Plateau, are thinner in the Bull Creek watershed. Typical soil thickness for sampling sites in this study are approximately 10 cm.

Bull Creek baseflow is provided by numerous springs and seeps discharging from the dissected limestone units. There are abundant karst features in the Edwards limestone, including epikarst, caves, sinkholes, and conduits that control groundwater flow in the area. Many Bull Creek tributaries are ephemeral, although water can almost always be found flowing in the main trunk. Typical baseflow is 0.06 m^3/s, as measured at a U.S. Geological Survey (USGS) gaging station (station number 08154700, Bull Creek at Loop 360) (USGS, 2014). Losing streams are commonly observed in areas underlain by Edwards limestone. The watershed is also prone to flash flooding.

2.2 URBANIZATION SETTING

Urbanization in the Bull Creek watershed is recent relative to urban development in Austin. Median structure age for the watershed is 1989, whereas the median structure age for the Waller Creek watershed is 1965 (Christian et al., 2011). An aerial mosaic of the upper Bull Creek area from 1947 shows sparse rows of rural pastures along two major roads as the only development at this time (Marquez, 1947; Appendix A). Many areas of this mosaic would later undergo substantial urban development. Today, the dominant land use category in the urbanized reaches is residential. There are also substantial contiguous areas that have remained rural, due in part to the designation of protected habitat for the endangered black capped vireo (Vireo atricapilla). Both parcel density and road density in the Bull Creek watershed provide visual confirmation of these development patterns (Fig. 3, Fig. 4)

Chapter 3: Methods

Sample collection and preparation methods described here for the most part follow the low-contamination protocol described in Christian et al., (2011).

3.1 Sample Collection

Field sampling for this study involved the collection of spring water, tributary water, municipal water, untreated wastewater, bedrock, and soil samples. Spring sites (n=12) and tributary sites (n=17) were each sampled no fewer than two times, (Table 5). Spring samples were collected between April 2011 and August 2012 for a survey of E. tonkawae by the City of Austin Watershed Protection Department. Field parameters were measured using a Hydrolab MiniSonde 5 Multiprobe SE. Tributary samples were collected throughout July, 2012 to June, 2013. Field parameters for these sites were measured with a MyronL Ultrameter 6PII-FCE. Bull Creek discharge was monitored by the USGS at site 08154700. Sampling was avoided for a few days after major storms so that streamwater was collected under baseflow conditions, as shown by the position of the sample collection dates on the stream hydrographs from gauging site 08154700 (Fig. 7).

Spring and tributary samples were collected into separate vials for cation and strontium isotope analysis (spring samples unfiltered; tributary samples filtered through 0.45 µm acid-washed polypropylene filter; both sample types collected in acid-washed polypropylene vials and acidified to pH<2 with lab-distilled 7N HNO_3), anion analysis (unfiltered, stored in non-acid washed polypropylene vials), and alkalinity analysis (unfiltered, stored with zero headspace in non-acid washed glass amber vials). Prior to separation into the various vials, tributary samples were collected into 250 mL polypropylene bottles (that were pre-cleaned with Micro-90 cleaning solution) and stored below $4^{o}C$.

Municipal water was collected (n=7) from the restrooms of various businesses located within the Bull Creek watershed during spring and tributary sampling campaigns. Municipal water samples were collected using the same procedures as spring and tributary samples. Wastewater samples were collected by the City of Austin Watershed Protection Department in 2011 (City of Austin, 2012).

Limestone bedrock samples (n=8) were collected from exposed outcrops within the Bull Creek watershed. Soils (n=11) were collected from undisturbed sites with pre-washed plastic trowels. Each soil sample was collected from the top 5-15 cm of soil after scraping away the top 5 cm, with a collection volume of approximately 250 mL. Both soil and bedrock samples were stored in Ziploc bags.

3.2 Bedrock and Soil Processing

Bedrock samples were cut with a clean, water-cooled rock saw into pieces roughly the size of sugar cubes, with care taken to remove all exposed surfaces, and crushed with an agate mortar and pestle into a coarse powder. One sample was randomly chosen for a "weathered rind" comparison, where a second piece of the sample was crushed without the removal of the originally-exposed weathered rind, leaving roughly 30% rind coverage. Each powdered limestone sample was then leached with 1 M ammonium acetate (normalized to a pH of 8.2) for ten minutes to remove exchangeable Sr before dissolution with acetic acid for ten minutes. The limestone was then separated, and the acetic-acid solution was transferred into Teflon beakers for $^{87}Sr/^{86}Sr$ chemistry. One sample was chosen at random for a second acetic-acid leach performed without ammonium acetate pretreatment. The leaching procedure is a modified version of the procedures described in Montañez et al., (1996).

Soil leaching was performed by adding 1.5 grams of sample to 10 mL of 0.2 M ammonium acetate (normalized to a pH of 8.2) and agitating the samples at ten minute intervals for an hour. The tubes were then centrifuged and the supernatant was pipetted into a clean Teflon beaker for $^{87}Sr/^{86}Sr$ chemistry. A second aliquot of one sample chosen at random was leached according to the same procedure using water instead of ammonium acetate.

3.3 Analytical Methods

Ion concentrations for all samples collected before May 2012 (with the exception of wastewater Sr) were measured by the Lower Colorado River Authority, in partnership with the City of Austin Watershed Protection Department. All analytical data for samples collected after May 2012, as well as Sr concentration data for the CoA wastewater samples, were generated at the University of Texas at Austin (UT Austin). This section describes the methods performed at UT Austin.

Cation concentrations were measured using an Agilent Technologies 7500CE inductively coupled plasma quadrupole mass spectrometer (ICP-Q-MS). Samples were diluted 10x with 2% solution of trace metal grade nitric acid in millipore deionized water prior to analysis. Curve standards were prepared from certified aqueous cation standards and checked against SRM 1643e throughout each analytical sequence. SRM 1643e control samples (n=17) all measured within ±6% of their established values. Estimated 2σ uncertainty based on SRM 1643e analyses for Na, Mg, Ca, K, & Sr are all below 6%. Replicates (n=5) agree within ±5% for all reported cations, with the exception of Sr for one replicate at 16%. All samples that were spiked with an aliquot of SRM 1643e (n=6) measured within ±15% of their expected values for all reported cations with two exceptions, and 17 out of 24 were within ±5% of their expected values (Table 18).

Cl, SO_4, and NO_3 were measured using a Waters 501 high performance liquid chromatograph (HPLC) coupled to conductivity and absorbance detectors. Prior to analysis, all samples were sent through an ion exchange filter to replace divalent with monovalent cations for column preservation. Samples were injected into a sodium borate-gluconate eluent stream en route to column exchange. Fluoride was measured via LaF_3 ion selective electrode (FISE) after mixing sample aliquots 1:1 with TISAB II. Analytical curve standards were prepared for both instruments by dissolving salt powders in deionized water, and were compared against certified anion standards measured throughout the analytical sequences to demonstrate curve accuracy and monitor instrumental drift. All measured standards (n=14 for HPLC, n=9 for FISE) agree within ±10% of their published values. Laboratory replicates all agree within ±10% with the exception of one NO_3 measurement at -25%.

$^{87}Sr/^{86}Sr$ values were measured following the methods of Banner and Kaufmann (1994) using a Thermo Triton thermal ionization mass spectrometer (TIMS) operated in static multi-collection mode. Prior to analysis, Sr was isolated from each sample using Eichrom Sr-specific exchange resin. Post-ion-exchange sample aliquots were then mixed with Ta_2O_5 and loaded onto common-Re filaments. Laboratory blanks were measured by isotope dilution to assess contamination from the laboratory sample handling, ion exchange and filament loading procedures. Four laboratory blanks range from 1 to 9 pg, and a fifth at 32 pg. All laboratory blanks are four to five orders of magnitude smaller than a typical sample load. SRM-987 standards were analyzed at the beginning and end of each sequence (about 15 samples) to monitor TIMS accuracy. External 2-sigma (2σ) uncertainty based on SRM-987 analyses (n=24) is 0.000035.

Alkalinity measurements were titrated with certified 0.1 N H_2SO_4, either via manual titration with a Gilmont 2 mL micro-buret or auto-titration with an SM Titrino 702. Alkalinity values are reported as HCO_3.

Charge balance has been calculated for spring and tributary waters (n=79; Table 1), municipal water samples (n=7; Table 1), and wastewater samples (n=9; Table 1), neglecting the effects of neutral complex formation due to the low ionic strength of the samples in these groups. Charge balances for spring and tributary waters range from -0.8% to 10.3%, with 89% of samples between ±5%. Municipal water charge balance ranges from -1.1% to 3.6% for six out of the seven samples, with the seventh measuring at 10.7%. Wastewater charge balance ranges from -0.3% to 7.4%, with two samples measuring outside ±5%. All samples that fall outside the range of ±5% are positive, indicating that there is a cation dominance for these calculations.

Field blanks and lab blanks collected during the study measured below detection limits, or were insignificant when compared to the sample size (Table 24, Table 25). The majority of field lanks are below the limits of detection. ICP-Q-MS, HPLC, FISE, and titration blanks were < 10% of all associated samples with the exception of the field blank taken on March 7th, 2013. Elevated Ca and HCO_3 in this field blank are <10% of all associated spring and tributary water samples, but >10% of the associated tap water sample. Field blanks for Sr as measured by isotope dilution were between 5 and 138 pg, with the exception of the field blank taken on March 7th that measured at 5,529 pg. This elevated blank is 200× less than a typical sample load. No corrections were made to the ion composition $^{87}Sr/^{86}Sr$ measurements (n=5) associated with the elevated blank as the data quality is unlikely to be significantly impacted at such a low contaminant level.

A reconfiguration of Faraday cups on the TIMS in September 2013 caused a small but resolvable reduction in the mean value of SRM-987 $^{87}Sr/^{86}Sr$ measurements.

Before the reconfiguration, mean SRM-987 = 0.710264 (2σ=0.000019, n=24), whereas after, mean SRM-987 = 0.710220 (2σ=0.000013, n=3), representing a downward shift of 0.000044. Samples measured after the reconfiguration have been adjusted upwards by 0.000044 to reflect this offset, and are labelled in Table 1 and Table 12.

3.4 COMPUTATIONAL METHODS

Covariation of selected dissolved ions are examined, with charge balance and calcite saturation index ($SI_{calcite}$) (using the Guntelberg approximation) calculated for the aqueous sample types. Piper plot and Stiff diagram (Fig. 9; Fig. 10) were prepared using Aqqa software from Rockware.

Maps were prepared in ArcGIS using files received from the City of Austin, Texas Capital Area Council of Governments, and the Travis County Appraisal District. For each spring and tributary site in the Bull Creek watershed (29 sites total), a sub-watershed was delineated, so that each water sample site could be evaluated based on its respective bedrock unit(s), soil type(s), and extent of urban development. Watersheds for the individual springs and tributaries were delineated following Maidment (2002). Layer files for soil types, geologic units, road lines, and land use were clipped to each sub-watershed for comparison. Road density was calculated by dividing road length by total area. Impervious cover was estimated using approximations associated with various land use types in Austin. Median structure age was calculated for the sub-watersheds associated with the twelve spring sites.

Chapter 4: Results

Analytical results for spring, tributary, municipal water, wastewater, bedrock, and soil samples are presented in Table 1 and Table 2, and are summarized in Table 3, Table 4, Table 5, and Table 6, where a distinction is made between urban and rural locations for spring and tributary samples. Criteria for defining rural vs. urban are discussed in Section 4.3. Geospatial results are presented in Table 8 and Table 9.

4.1 AQUEOUS CHEMISTRY

Water samples collected from springs and tributaries in the Bull Creek watershed (n=79) are Ca-HCO_3 waters (Fig 8; Fig 9). Ca concentrations range from 67-166 ppm and HCO_3 concentrations from 212-481 ppm. $SI_{calcite}$ ranges from −0.447 to 0.890. Magnesium concentrations range from 11-33 ppm. Ca, Mg, and HCO_3 are expected to be the dominant constituents for surface water and groundwater in contact with limestone bedrock where both calcite and dolomite are present (Apello and Postma, 2005).

Municipal water samples collected within the Bull Creek watershed (n=7) have markedly lower concentrations and smaller ranges of Ca and HCO_3 when compared to Bull Creek spring and tributary samples. Ca concentrations range from 11-12 ppm and HCO_3 concentrations from 60-76 ppm. $SI_{calcite}$ varies between 0.253-0.503. Low concentrations of Ca and HCO_3, as well as the relatively high pH (9.2-9.4) of municipal water, are attributed to water softening during municipal treatment. Municipal water is classified as Mg-HCO_3 water (Fig 9; Fig 10), with Mg ranging from 14-18 ppm.

Wastewater samples from the Austin area (n=9) represent a product of local municipal water, and were sampled from the underground sewer pipe network before treatment at a wastewater plant. Ca concentrations range from 15-37 ppm, HCO_3 from

94-166 ppm, and Mg from 16-21 ppm. $SI_{calcite}$ was not calculated for Austin area wastewater samples because pH data are not available.

As a trace element in limestone, Sr is a minor constituent of water from Bull Creek springs and tributaries, ranging in concentration from 0.13-4.9 ppm. An alkaline earth element with solubility akin to Ca, Sr concentrations are also relatively low in softened municipal water, with concentrations ranging from 0.11-0.13 ppm. Wastewater Sr concentrations ranged from 0.12-0.40 ppm. Two rainwater samples collected on the roof of the Jackson Geology Building (JGB) in May and June of 2013 have Sr concentrations of 0.07 and 0.19 ppb, respectively.

Elevated concentrations of Na and Cl in water samples are herein considered to be associated with the impacts of urbanization. Christian et al. (2011) reports a seven-fold increase in Na concentration (10 ppm vs. 70 ppm) and a five-fold increase in Cl concentration (18 ppm vs. 88 ppm) when comparing streamwater from rural and urban Austin watersheds. Na concentrations for spring and tributary samples in the Bull Creek watershed range from 7-74 ppm, and Cl from 16-94 ppm. Among all spring and tributary samples, Na and Cl provide the strongest correlation of all major dissolved ions (r^2 = 0.88, $p < 0.0001$; Table 11). In municipal water samples, Na concentration ranges from 18-31 ppm and Cl from 27-44 ppm, whereas Na concentration ranges from 43-105 ppm and Cl from 57-176 ppm in wastewater samples.

F is added to municipal water by the City of Austin. Dissolved F ranges from 0.56-0.79 ppm in municipal water samples, and from 0.41-1.2 ppm in wastewater samples. Spring and tributary samples range from 0.08-0.46 ppm for F concentrations.

4.2 ^{87}Sr/^{86}Sr Results

^{87}Sr/^{86}Sr values for tributary and spring samples range from 0.70769 to 0.70875 (n=54). Austin municipal water values range from 0.70910 to 0.70952 (n=7), which are the highest values for any sample type. This range compares with a range of 0.70878 to 0.70906 for municipal water analyzed in 2002 and 2003 (Christian et al; 2011) and City of Austin municipal water samples collected in 2010 and 2011 for another study, which range from 0.70896 to 0.70918 (Snatic, 2013). Wastewater ^{87}Sr/^{86}Sr values vary from 0.70794 to 0.70899 (n=9).

^{87}Sr/^{86}Sr values for bedrock samples (leachates) range from 0.70760 to 0.70782 (n=10) and provide the lowest values of any sample type. Soil leachates are divided into two groups based on urban irrigation: 1) non-irrigated sites, with low ^{87}Sr/^{86}Sr values, from 0.70785 to 0.70835 (n=9) and, 2) irrigated sites, with high ^{87}Sr/^{86}Sr values from 0.70870 to 0.70913 (n=3).

^{87}Sr/^{86}Sr for the bedrock sample that was not pretreated with ammonium acetate before leaching is 0.70769, while the pretreated leachate from the same sample measures at 0.70766. ^{87}Sr/^{86}Sr for the bedrock sample that was leached without the removal of the weathered rind is 0.70775, while the same sample that was measured with the weathered rind completely removed is 0.70777. The two samples subject to alternate leaching procedures fall outside ±2σ uncertainty when compared to their respective analogs, however in both cases they bear considerable resemblance to their respective analogs. The effects of removing the exchangeable fraction of Sr and removing the weathered rind appear to be minimal.

^{87}Sr/^{86}Sr for the soil sample leached with water is 0.70785, while the same sample that was subjected to leaching with ammonium acetate also measures 0.70785. These samples both fall within ±2σ uncertainty of one another.

4.3 Geospatial Results

Impervious cover estimates for the 29 sub-watersheds associated with the spring and tributary sites range from 1% to 62%. Road density varies between 0 and 0.018 km^{-1} (road length divided by total area). Median structure age for the sub-watersheds associated with the springs ranges from 1971 to 2003. Among the eight watersheds studied by Christian et al. (2011), median structure age ranges between 1965 and 1991.

Road density and impervious cover estimates for the individual sub-watersheds associated with spring and tributary sample sites provides a threshold for designating sites as either rural or urban. By comparing these urbanization measures with aerial photography from the various sites, I designate sub-watersheds with estimated impervious cover $\leq$ 25% and road density $\leq 2 \times 10^{-3}$ m^{-1} as rural. Sub-watersheds with either impervious cover or road density levels above these threshold values are classified as urban. Of the 29 designated sub-watersheds, seven are designated as rural and 22 as urban (Table 9).

4.4 Subdivision of Urban Sites Based on Sr Concentration and $^{87}Sr/^{86}Sr$

I further subdivide the urban stream-water samples (n=22) into two subgroups based on Sr concentrations: low-Sr concentration (Sr $\leq$ 0.27 ppm; n=8) and high-Sr concentration (Sr $\geq$ 0.44 ppm; n=14). No samples have concentrations between 0.27 and 0.44 ppm (Table 1). Additionally, rural samples were subdivided in the same fashion, with six sites in the high-Sr concentration group and one site in the low-Sr concentration group.

The urban streamwater samples demonstrate an inverse relationship between Sr concentration and $^{87}Sr/^{86}Sr$ values. Samples from the low-Sr concentration group are characterized by high $^{87}Sr/^{86}Sr$ while the high-Sr concentration samples are accompanied by low $^{87}Sr/^{86}Sr$ (Table 1). Although there is some overlap between the $^{87}Sr/^{86}Sr$ ranges for the low-Sr and high Sr groups the separation is evident. All urban spring and tributary samples with $^{87}Sr/^{86}Sr \geq 0.70830$ have Sr ≤ 0.21 ppm (n=18), while all urban spring and tributary samples with $^{87}Sr/^{86}Sr \leq 0.70800$ have Sr ≥ 0.44 ppm (n=15; Table 1).

Christian et al. (2011) analyzed six streamwater samples that were collected from the Bull Creek watershed during August, 2002. Sr concentration for these samples ranges from 0.64 to 1.94 ppm, and $^{87}Sr/^{86}Sr$ ranges from 0.70780 to 0.78724. These samples all fall in the high-Sr concentration group and have relatively low Sr, which is consistent with both the Sr and $^{87}Sr/^{86}Sr$ trends in the sample group used for the this Bull Creek study.

Chapter 5: Discussion

The differences in ion composition and $^{87}Sr/^{86}Sr$ between spring and tributary waters are herein examined in order to account for the effects of leaked anthropogenic water on streamwater chemistry. The ion composition and $^{87}Sr/^{86}Sr$ of water from rural springs and tributaries is considered to be reflective of interaction with natural bedrock and soil endmembers. The rural water samples provide a baseline for comparison with water from urban spring and tributary sites.

5.1 Representativeness of Spring and Tributary Samples

Sampling frequency was designed to address the potential effect of short-term variations in Bull Creek streamwater chemistry. Four of the tributary sites (AS, FE, FN, MV; Fig. 3) were sampled repeatedly between July 2012 and June 2013, providing six or seven samples from each site (Table 1). The major ion concentrations of samples from each of these tributary sites were relatively consistent throughout the one year period (Table 1). $^{87}Sr/^{86}Sr$ was correspondingly measured at one of these sites (site FN; n=7) and was consistently between 0.70848 and 0.70858. Six out of seven of these values fall within the analytical uncertainty range constrained by the mean value $\pm$ 2 $\times$ standard deviation. Spring sites were sampled between August 2010 and April 2011, with up to two samples collected at each site. Much like the tributaries samples, the geochemistry at the spring sites was relatively consistent for major ion concentrations and $^{87}Sr/^{86}Sr$ values (Table 1). Sample representativeness is also addressed by Christian et al. (2011), where 42 samples were collected from the same site in Waller Creek at a gauging weir on the campus of the University of Texas at Austin and analyzed for $^{87}Sr/^{86}Sr$ values; 93% of these were within the mean $\pm$ 2 $\times$ standard deviation, which ranges from 0.70858 to 0.70906.

Previous studies of karst spring response to precipitation have demonstrated a compositional shift in the ionic load carried by spring discharge immediately following rainfall with a gradual return to pre-recharge conditions (Lee & Krothe, 2001; Perrin at al., 2003; Doctor et al., 2006). A compositional shift in springwater geochemistry has been demonstrated for Barton Main Spring in Austin (USGS site 08155500) during a study conducted from November 2008 to March 2010, in response to changes in hydrologic conditions from a dry interval to a wet interval (Wong et al., 2012.) In contrast, the Bull Creek samples were collected under baseflow conditions (Fig. 7) and exhibit little geochemical variability. Because of this and the lack of geochemical variability in the inter-seasonal time series samples from tributary site FN , it is likely that the results presented here do not reflect short-term trends or seasonality.

5.2 GEOCHEMICAL COMPARISON OF URBAN AND RURAL SAMPLE GROUPS

A comparison of ion concentrations for samples from urban and rural sites indicates that urban sites have approximately three times as much Na and Cl relative to rural sites (Table 3; Table 4, Fig. 10). K, SO_4, F, and NO_3 concentrations were also elevated in samples from urban sites (Table 3; Table 4).

Elevated concentrations of Na and Cl in urbanized Bull Creek springs and tributaries is consistent with a 1999-2000 City of Austin study, which also classified Bull Creek streamwater sites as urban or rural based on impervious cover estimates (Geismar, 2001). Geismar (2001) notes Na concentration from 32-56 ppm at urban sites and 7-12 ppm at rural sites (Geismar, 2001). My results indicate similar values with a slightly lower mean Na concentration for urban sites (31 ppm) and a mean Na concentration of 10 ppm for rural sites (Table 3; Table 4). Similar consistencies between the two studies are demonstrated by Cl and K concentrations (Table 3; Table 4). A study of the ionic composition of six water samples taken from tributary site MV (Fig. 3) between October 1992 and December 1993 demonstrates that site MV has had elevated Na and Cl dating back over 20 years (Ging, 1995). Na for the samples taken between 1992 and 1993 ranges from 18-48 ppm and Cl from 38-66 ppm, whereas the water samples collected from Site MV during 2012-2013 have Na ranging from 29-38 ppm and Cl from 45-57 ppm. A survey of Bull Creek conducted in 1982 (Texas Department of Water Resources, 1982) also sampled streamwater at site MV and found chloride to be 42 ppm, signifying that elevated levels of Cl have been associated with site MV for over 30 years.

Time-series for Na and Cl concentrations for urban site TB and rural site PN (Fig. 3) between April 1996 and April 2011 (data from City of Austin), indicate how urbanization can affect water quality on a decadal scale (Fig. 11; City of Austin, 2014). At the beginning of the time series, both sites had similar concentrations of Na and Cl. The rural site maintained relatively low concentrations throughout the 15 year period. At the urban site, however, both Na and Cl concentrations increased steadily, effecting a two-fold increase over 15 years.

5.3 SOURCES OF SR IN THE BULL CREEK WATERSHED

Sources of Sr in the Bull Creek watershed that may contribute to streamwater compositions are bedrock, soil (subdivided into irrigated soil and non-irrigated soil), and leaked anthropogenic water. Rainwater is not considered a significant source of Sr because the Sr concentration of rainwater is at minimum three orders of magnitude lower than all other aqueous sample types.

Both bedrock and non-irrigated soil are sources of Sr with low $^{87}Sr/^{86}Sr$ (Table 5; Table 6; Fig. 12). The low bedrock values reflect $^{87}Sr/^{86}Sr$ in Cretaceous seawater. Soil samples collected at non-irrigated sites represent the natural soil in the watershed, unaltered by urban development. The thin nature of these soils may, in part, account for their consistently low $^{87}Sr/^{86}Sr$ values, as a connection has been established in central Texas between soil horizon depth and $^{87}Sr/^{86}Sr$ values (Cooke et al., 2007). By comparison, the greater Austin area encompasses both the thin soils along the uplifted Edwards Plateau (like those found in Bull Creek) as well as thicker soils on the Blackland Prairie to the east.

Municipal water, wastewater and irrigated soil are sources of Sr with high $^{87}Sr/^{86}Sr$ in Bull Creek streamwater. The high values in municipal water are reflective of water-rock interaction between the Colorado River and Precambrian granites of the Llano Uplift, upstream of Austin. Leachates from the irrigated soils had much higher $^{87}Sr/^{86}Sr$ than the non-irrigated soil samples (Table 5; Table 6; Fig. 12). The irrigated soils have $^{87}Sr/^{86}Sr$ values that are similar to municipal water, which suggests that municipal water used for irrigation has contributed to the potential source of Sr from these soils.

Wastewater samples were collected from manholes around the Austin area and have a relatively wide range of $^{87}Sr/^{86}Sr$ (Table 5; Table 6; Fig. 12). Wastewater composition reflects the initial composition of municipal water and its evolution due to anthropogenic use. Many of the wastewater samples have relatively low $^{87}Sr/^{86}Sr$ values, lower than those of municipal water. These results are somewhat counterintuitive, given the high $^{87}Sr/^{86}Sr$ values for municipal water. One hypothesis to account for these data is that a compromised wastewater pipe structure may provide a drainage conduit for groundwater in the vadose zone, mixing groundwater in contact with limestone (and thus having low $^{87}Sr/^{86}Sr$ values reflective of dissolution of this limestone) into the pipes with wastewater.

Irrigated soils and wastewater are herein referred to as discrete endmembers that contribute to streamwater evolution, although both endmembers have municipal water as a likely source of Sr. Although each of these endmembers has the potential to contribute high $^{87}Sr/^{86}Sr$ to Bull Creek streamwater, the ultimate source of high $^{87}Sr/^{86}Sr$ is municipal water from the Colorado River.

Spring and tributary samples from rural sites all had relatively low $^{87}Sr/^{86}Sr$ values, representative of water-rock interaction with local bedrock and non-irrigated soils (Table 5; Table 6, Fig. 12). Christian et al. (2011) establishes that streamwater collected from rural watersheds in Austin has low $^{87}Sr/^{86}Sr$ akin to the $^{87}Sr/^{86}Sr$ in rural spring and tributary waters from Bull Creek. A study examining travertine deposits in the West Bull Creek watershed (a rural watershed bordering the Bull Creek watershed; Fig. 2) demonstrates that groundwater mean $^{87}Sr/^{86}Sr = 0.70799$ (DeMott, 2007). My findings for $^{87}Sr/^{86}Sr$ in rural spring and tributary waters are consistent with both of these studies. Similarly, the low $^{87}Sr/^{86}Sr$ values for urban spring and tributary samples from the high-Sr concentration group likely reflects water-rock interaction with low $^{87}Sr/^{86}Sr$ bedrock and soil endmembers. However, high $^{87}Sr/^{86}Sr$ values for low-Sr concentration urban spring and tributary samples cannot be explained by Sr sources from bedrock or ion-exchange with non-irrigated soils. Rather, the $^{86}Sr/^{86}Sr$ in these samples can be explained by contributions from anthropogenic water and irrigated soil.

Snatic (2013) proposes soils as a source of radiogenic Sr to urban streamwater by demonstrating a geographic correspondence between streamwater $^{87}Sr/^{86}Sr$ and mapped soil units, as well as a shift in Mg/Ca that corresponded to a transition in soil moisture conditions. Higher Mg/Ca is associated with a longer groundwater residence time in limestone environments (Wong et al., 2011). Snatic (2013) demonstrates that both Mg/Ca and $^{87}Sr/^{86}Sr$ in streamwater are higher during a period of drought than during a relatively wet period. Although no systematic shift in Mg/Ca ratios or $^{87}Sr/^{86}Sr$ values in spring and tributary samples is observed in this study, the high $^{87}Sr/^{86}Sr$ values for irrigated soils suggests this endmember is a likely source for high $^{87}Sr/^{86}Sr$ values observed in some of these streamwater samples. Nonetheless, anthropogenic water is the most likely contributor of radiogenic Sr to urban spring and tributary samples with high $^{87}Sr/^{86}Sr$ values. This conclusion is based on the observations that 1) municipal water has very low Sr concentrations and high $^{87}Sr/^{86}Sr$ values, and 2) all of the urban spring and tributary samples with high $^{87}Sr/^{86}Sr$ values are in the low-Sr concentration group (Table 1; Fig. 13).

As a municipal water additive, F concentrations provide supporting evidence that municipal water contributes to urban stream flow in Bull Creek springs and tributaries. Although F concentrations and $^{87}Sr/^{86}Sr$ values respond differently to processes that govern the geochemical evolution of streamwater (e.g. dilution, water-rock interaction, evapotranspiration), overall one would expect samples with high $^{87}Sr/^{86}Sr$ values (the low-Sr concentration group) to have higher F concentrations than samples with low $^{87}Sr/^{86}Sr$ values (the high-Sr concentration group), and to have higher F concentrations than rural samples. In general, these relationships were observed for spring and tributary samples (Fig. 14). Mean F concentration for samples from the low-Sr concentration group was 0.28 ppm, 0.18 ppm for the high-Sr concentration group, and 0.14 ppm for the rural sample group.

The relationship between $^{87}Sr/^{86}Sr$ and 1/Sr is useful to graph because two-endmember mixing plots as a straight line, and quantifying the relative inputs from each endmember can be easily determined. $^{87}Sr/^{86}Sr$ vs 1/Sr variations for urban, rural, municipal, and wastewater samples demonstrate that samples from the low-Sr concentration group fall on/along a mixing line between a municipal water sample and a rural spring water sample (Fig. 13). The contribution from municipal water is generally between 50% and 90% based upon how samples plot along the given mixing line. This mixing line is included as an example; it would also be appropriate to draw mixing lines between wastewater samples and rural streamwater samples.

Discharge was gauged at site FN (a site with relatively high $^{87}Sr/^{86}Sr$) to be 0.0028 m^3/s (0.1 ft^3/s). This represents a daily total of 245,000 liters passing through this stream. At 90% municipal water contribution, the calculated contribution from municipal water is 221,000 liters per day at site FN, which is 0.1% of the 223 million gallons lost by the city municipal system daily.

In Section 5.3, above I note that one rural sample (from site LR; Fig. 3) is within the low-Sr concentration group, which is indicative of anthropogenic water input. With the exception of Sr concentration, the geochemical composition of samples collected at site LR was similar to other rural-group samples (Table 9, Table 1). Among all spring and tributary sites that are characterized by low Sr concentration (8 urban sites and 1 rural site), rural site LR has the lowest $^{87}Sr/^{86}Sr$ value (Table 1). The sub-watershed for site LR, however has the most impervious cover (25%) of any rural sample site. Water samples collected at this site have the lowest Sr concentration and the highest $^{87}Sr/^{86}Sr$ value among the rural sample group (Table 9, Table 1). As the rural site that has experienced the most urbanization, it is not unexpected to find some geochemical indicators of anthropogenic water influx in the spring water samples from site LR.

5.4 ANTHROPOGENIC WATER EVOLUTION IN THE NATURAL SYSTEM

As stated in section 5.3, the indicated contribution of municipal water to urban springs and tributaries is 50-90% based on the $^{87}Sr/^{86}Sr$ vs 1/Sr mixing model (Fig. 13). However, applying mixing lines in $^{87}Sr/^{86}Sr$ vs 1/Sr space to quantify the amount of anthropogenic water input to streamwater in urban springs and tributaries is limited because fluid mixing and water-rock interaction have similar trends. This is illustrated by the overlap between the arrow representing the evolution of municipal water dissolving limestone and the fluid-mixing line (Fig. 13). Christian et al. (2011) uses a mixing model that compares $^{87}Sr/^{86}Sr$ with (Na+Cl)/(Ca+HCO_3) to implicate anthropogenic water influx into natural streamwater as control on streamwater chemistry in Austin. This model suggests that streamwater from Waller Creek, which drains the most urbanized watershed in Austin, is reflective of at least 90% municipal water influx during baseflow conditions (Christian et al., 2011). Because dissolved Sr, Ca, and HCO_3 are not conservative measurements with respect to dissolution and precipitation of calcite, both the $^{87}Sr/^{86}Sr$ vs. 1/Sr mixing model from this study and the $^{87}Sr/^{86}Sr$ vs. (Na+Cl)/(Ca+HCO_3) mixing model from Christian et al. (2011) are subject to interference by these processes.

Although Christian et al. (2011) indicates anthropogenic water mixing with rural streamwater is a primary process governing the evolution of streamwater in Austin, I find substantial evidence that water-rock interaction between leaked anthropogenic water and local limestone bedrock is a controlling process on streamwater evolution. This is evident when comparing the various sample groups on a plot of Ca vs. Sr (Fig. 15). Added to this plot is a trend line for municipal water samples dissolving central Texas limestone with a representative Sr concentration. This line passes through nearly all samples from the low-Sr concentration group, indicating that limestone dissolution by municipal water can account for the compositional variability of the low-Sr group. Mixing between rural streams and anthropogenic endmembers cannot account for the overall variability in urban sample Ca and Sr compositions, thus mixing alone cannot account for the evolution of urban streamwater. To my knowledge, this is the first demonstration and discussion of how anthropogenic water, when transmitted into a natural system, follows the natural progression of water-rock interaction, evolving via a similar process that naturally recharged groundwater evolves.

The influence of water-rock interaction on Sr concentrations and $^{87}Sr/^{86}Sr$ values in Bull Creek streamwater adds new caveats to the use of these measurements for identifying and quantifying anthropogenic water inputs to natural streamwater. Anthropogenic water that escapes the pipe network and dissolves enough limestone will no longer contain the high $^{87}Sr/^{86}Sr$ values that characterize the anthropogenic water endmember. When considering high Na and Cl concentrations, as indicators of urban impacts on streamwater quality at urban spring and tributary sites, it is apparent that spring and tributary water samples with low $^{87}Sr/^{86}Sr$ may have anthropogenic water contributing to their composition. Similarly, recently leaked anthropogenic water with high $^{87}Sr/^{86}Sr$ values would not have yet dissolved sufficient limestone to resemble natural streamwater in composition; higher $^{87}Sr/^{86}Sr$ values may indicate that less reaction progress has occurred, potentially translating to relatively short residence time in the subsurface and/or spatial proximity to the compromised water infrastructure. These results indicate that $^{87}Sr/^{86}Sr$ values may provide a useful indicator of point sources of leakage from urban infrastructure.

5.5 CASE STUDY: FLORAL PARK

A highly-urbanized sub-watershed provides a promising setting for scaling down the streamwater quality study even further. The perennial tributaries in Floral Park (sample sites FB, FE, FN; Fig. 3) represent the headwaters of a larger tributary system in the Bull Creek watershed that extends roughly five kilometers downstream. Floral Park includes both perennial and ephemeral streams, and gaining and losing stream sections associated with fractured limestone bedrock.

All four of the tributary sample sites in Floral Park are characterized by contributions from anthropogenic water based on Sr concentrations and $^{87}Sr/^{86}Sr$ values

(Table 1). Although these sites are in close proximity, within a couple hundred meters of each other, they all have different $^{87}Sr/^{86}Sr$. (Table 1). Mixing models between anthropogenic water and rural streamwater would indicate that they are characterized by differing amounts of anthropogenic water contribution. Because water-rock interaction between leaked anthropogenic water and limestone is a likely process governing streamwater evolution, tributaries in Floral Park are likely receiving anthropogenic input from the same source, with differences in their chemistry related to different subsurface flow paths for each respective tributary (e.g. flow length, residence time).

Because municipal water and wastewater both impart high $^{87}Sr/^{86}Sr$ into the natural streamwater environment, it is necessary to use other measurements to distinguish these endmembers from one another. When compared to municipal water, wastewater has substantially higher levels of Cl and Na. Because sites FE, FN, and FB all have Na and Cl within the range of municipal water, the municipal endmember (and not the wastewater endmember) is inferred as the source of anthropogenic water for these sites.

Chapter 6: Conclusions

To evaluate the processes by which urbanization impacts streamwater in Austin, Texas, I examine the geochemical and isotopic composition of spring and tributary samples collected from rural and urban reaches of the Bull Creek watershed from August 2010 to June 2013, for comparison with local bedrock, soil, municipal water, and wastewater samples.

Elevated levels of Na and Cl concentrations at nearly all urban sites, when compared to rural sites, indicate that urbanization substantially impacts streamwater quality in the Bull Creek watershed. Examination of $^{87}Sr/^{86}Sr$ values and Sr concentrations for the Bull Creek streamwater samples indicates that anthropogenic water is a likely contributor of baseflow to springs and tributaries in urbanized reaches of Bull Creek. A principal conclusion of this study is that leaked anthropogenic water evolves via water-rock interaction with local bedrock, altering its composition along similar pathways that natural recharge is altered. Because this evolution will modify the isotopic composition of leaked anthropogenic water to resemble that of naturally recharged groundwater, this isotopic measurement may have potential to investigate the point-source nature of anthropogenic recharge.

The inferences made by this research are attained by examining the same urbanization trends across multiple scales. An approach focused on a single watershed (Bull Creek) with a large range in urbanization to address a hypothesis developed with city-wide data from Christian et al. (2011) minimizes regional geologic variation associated with a larger sample area. This Bull Creek study provides an example of how scale can be effectively manipulated to test existing hypotheses, as here I have shed new light on the processes governing streamwater evolution in the urban landscape.

Figures and Tables

Figure 1: The Edwards Aquifer region of Texas, with county borders appearing as faint gray lines. The northern segment of the aquifer is situated north of Austin. The "Catchment Area" on the map is for the San Antonio segment (Texas Water Resources Institute, 2012).

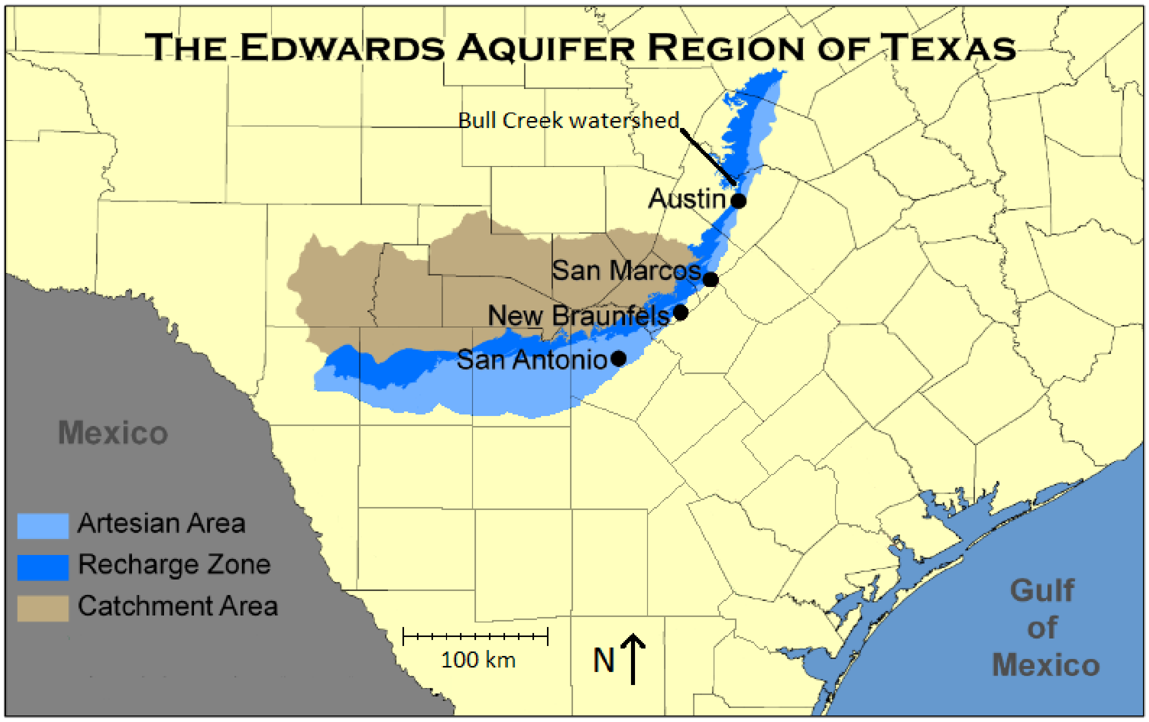


Figure 2: Map of Austin with the boundaries of the eight watersheds studied in Christian et al. (2011) (dark black lines). Major roads for the city appear as faint lines, gray for the areas not included in the study, and colored for emphasis inside the studied watersheds. The red square marks the location of downtown Austin. From Christian et al. (2011).

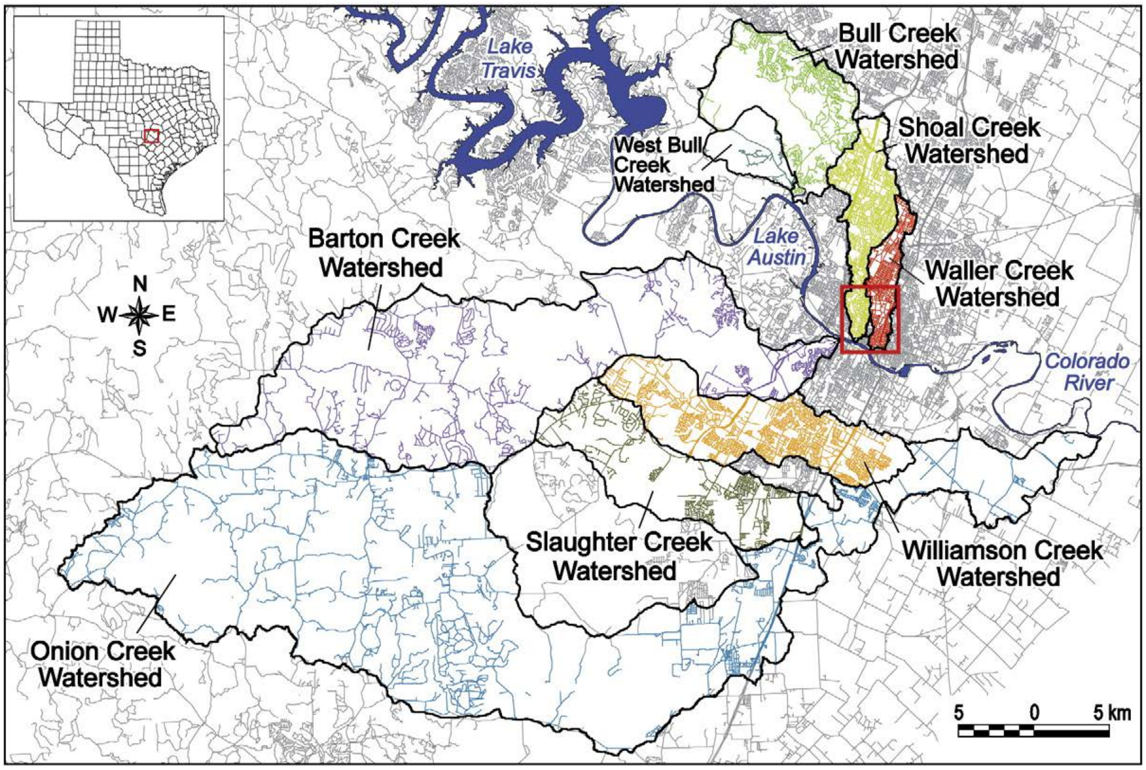


Figure 3: The Bull Creek watershed, including sample locations collected in this study, sample sites from Christian et al. (2011), major roads, and creeks.

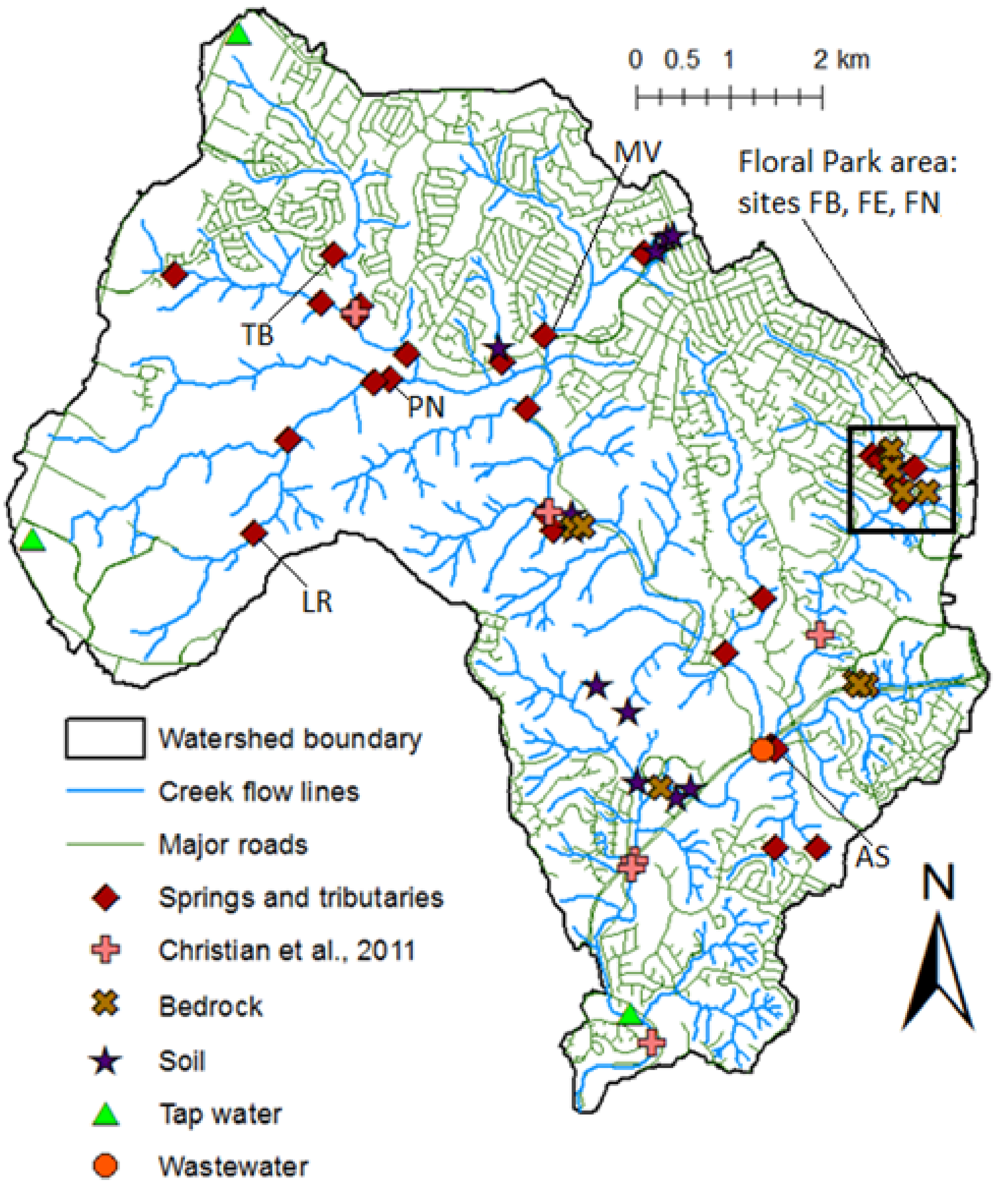


Figure 4: Property lines within the Bull Creek Watershed. (City of Austin, 2014)

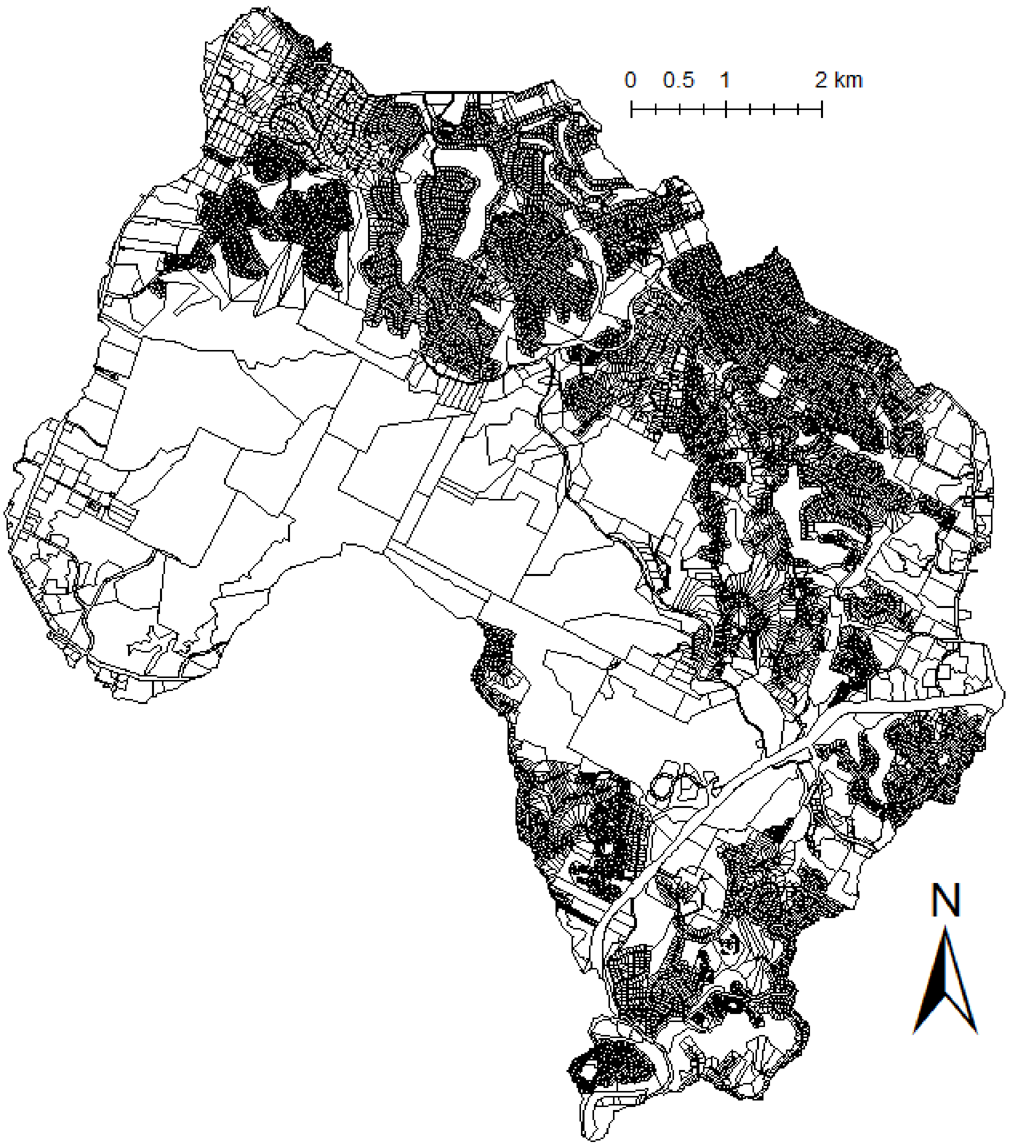


Figure 5: Bedrock exposures in the Bull Creek watershed, modified from Garner and Young (1976).

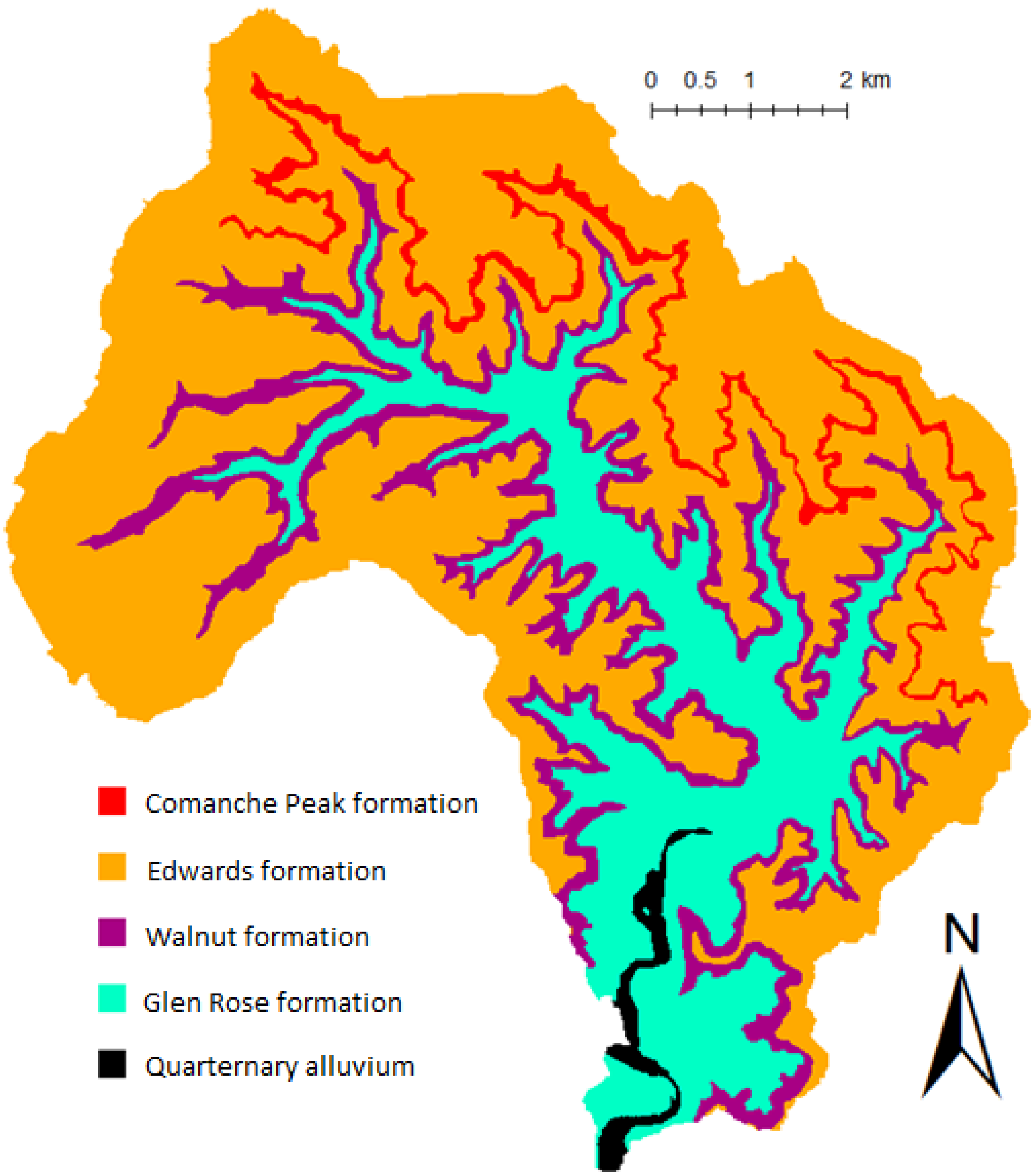


Figure 6: Soil exposures in the Bull Creek Watershed organized into the four dominant soil classes. Areas labelled as *Other* along the northern border of the watershed are part of Williamson County, and are categorized using a different classification scheme than the rest of Bull Creek, which is situated in Travis County (United States Natural Resource Conservation Service, 1997).

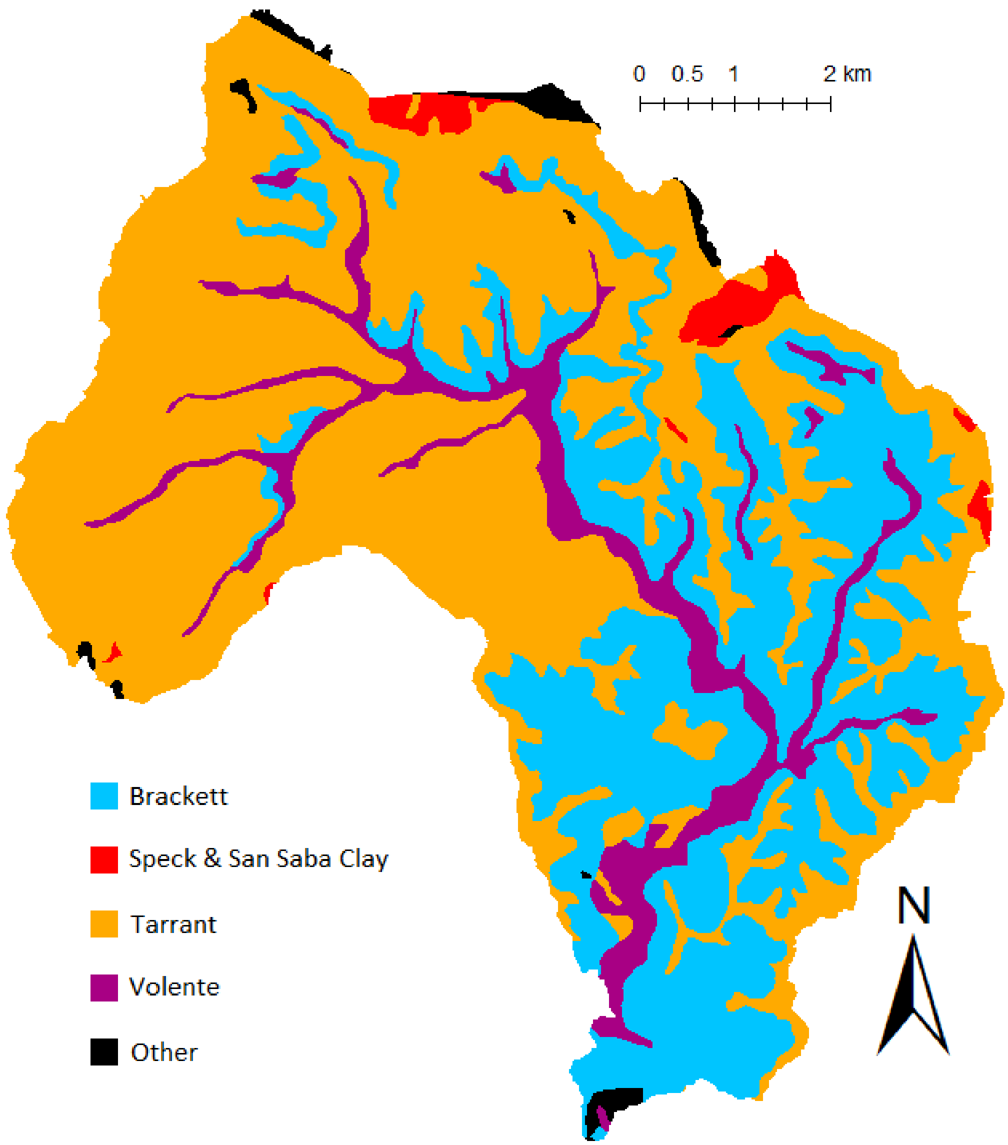
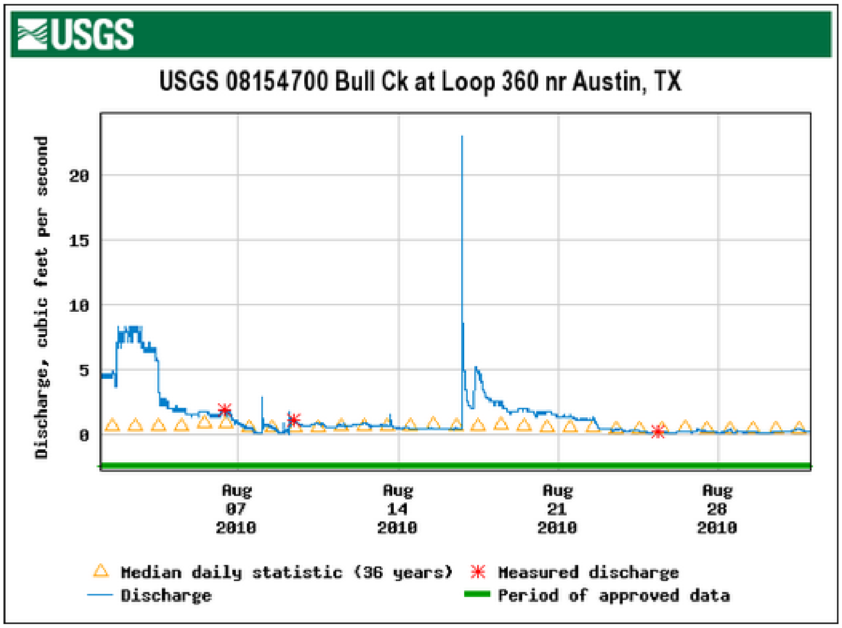
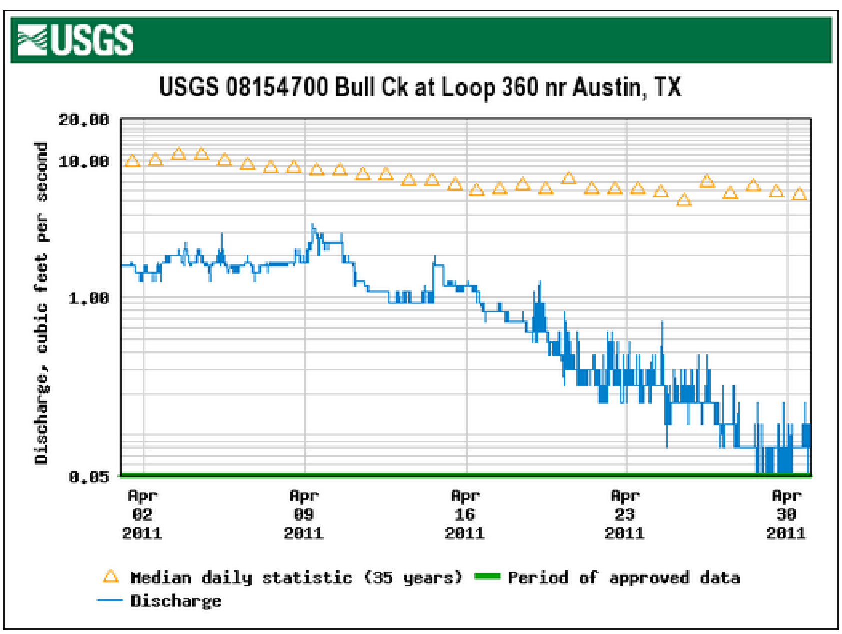


Figure 7: Bull Creek discharge hydrographs from USGS gauging site 08154700 (Bull Creek at Loop 360), for the months when water sampling was conducted in Bull Creek. Collection dates are also given below each graph, followed by median discharge for that day in cubic feet per second. 1 $ft^3/s = 0.028\ m^3/s$ (United States Geological Survey, 2014)

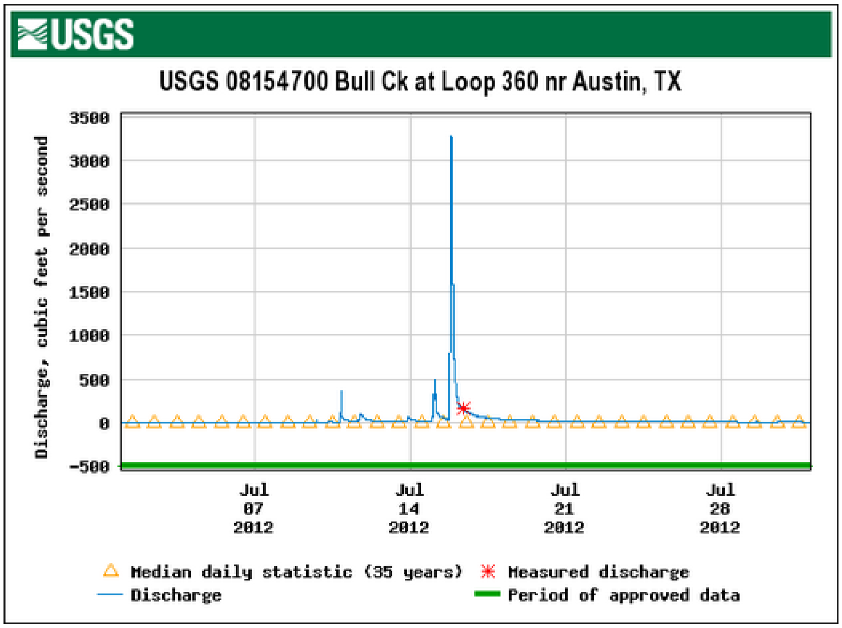


August 19th - 1.8; August 24th - 0.2; August 28th - 0.2; August 29th - 0.2

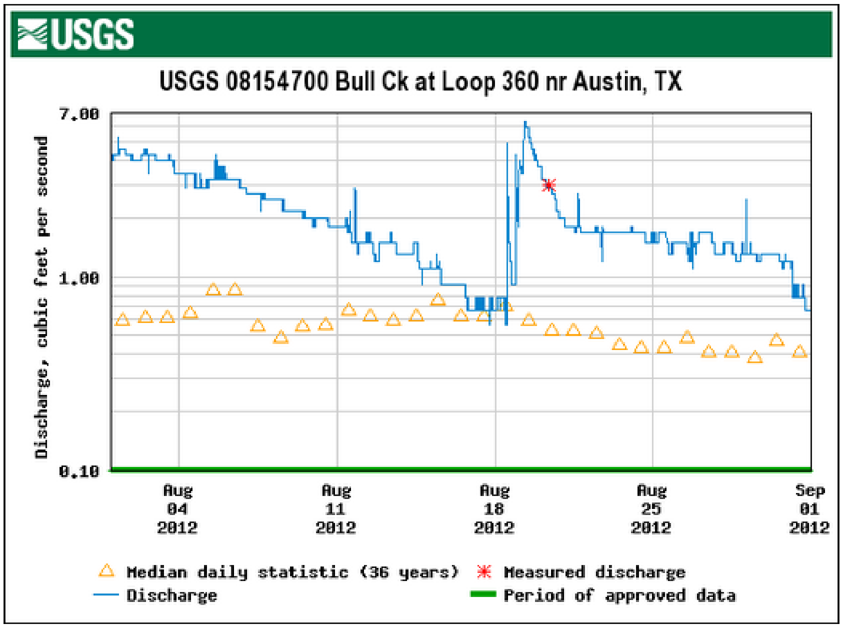


April 12th – 1.1; April 15th – 1.2; April 22nd – 0.3

Figure 7 (cont.)

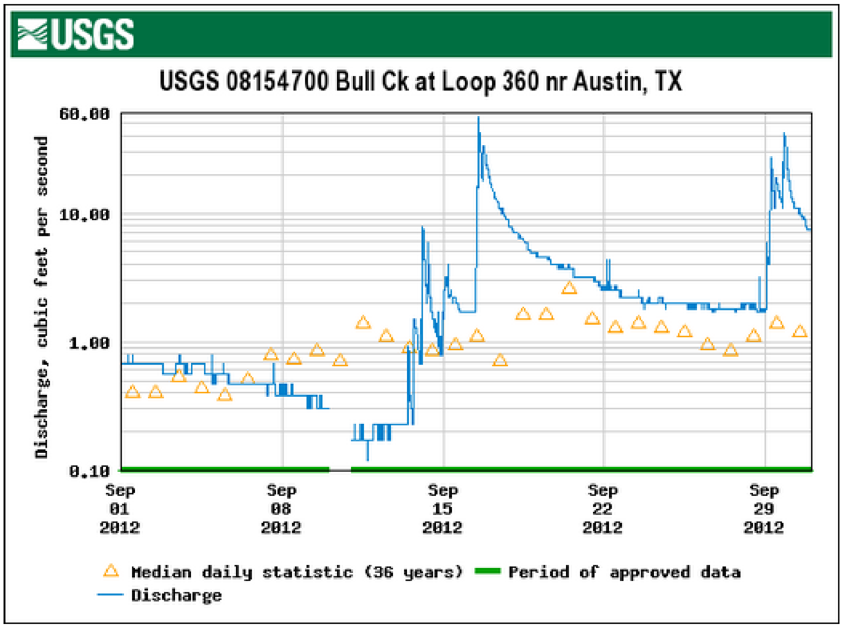


July 24th – 9.7; July 27th – 6.7

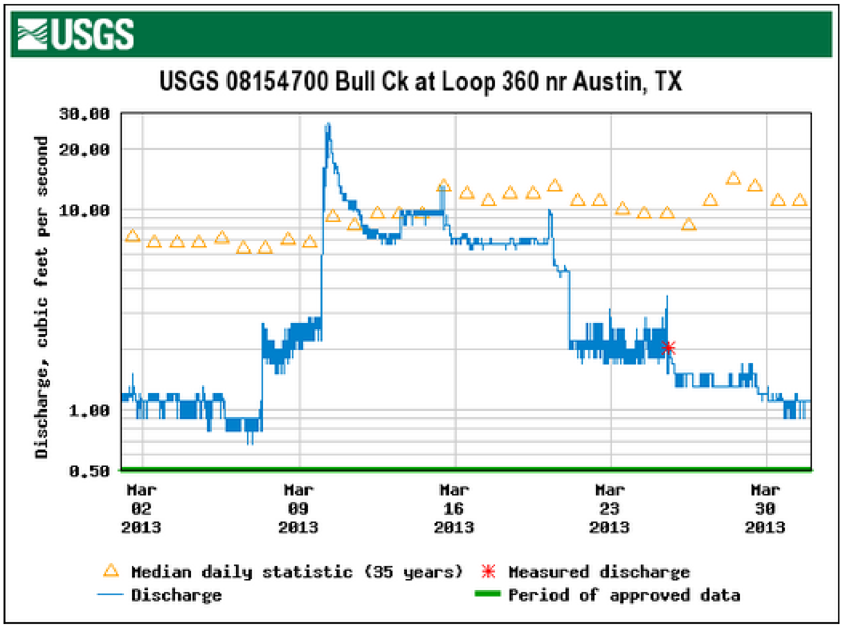


August 10th – 2.0

Figure 7 (cont.)

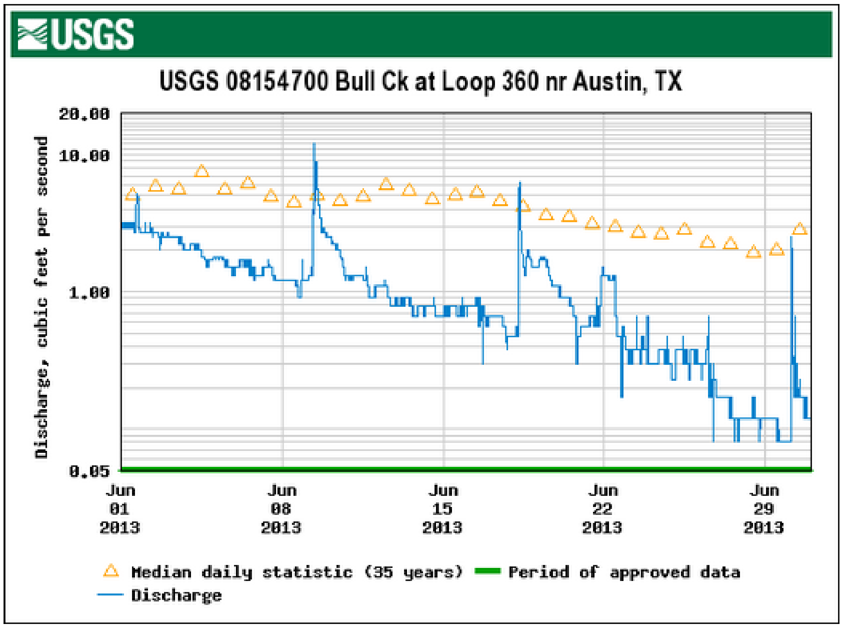


September 25th – 2.0



March 7th – 1.8

Figure 7 (cont.)



June 21st – 0.7

Figure 8: Ternary diagram (Piper plot) for Bull Creek spring and tributary samples, divided by rural and urban classifications along with City of Austin municipal water from the Bull Creek watershed (municipal) and wastewater from the greater Austin area (waste).

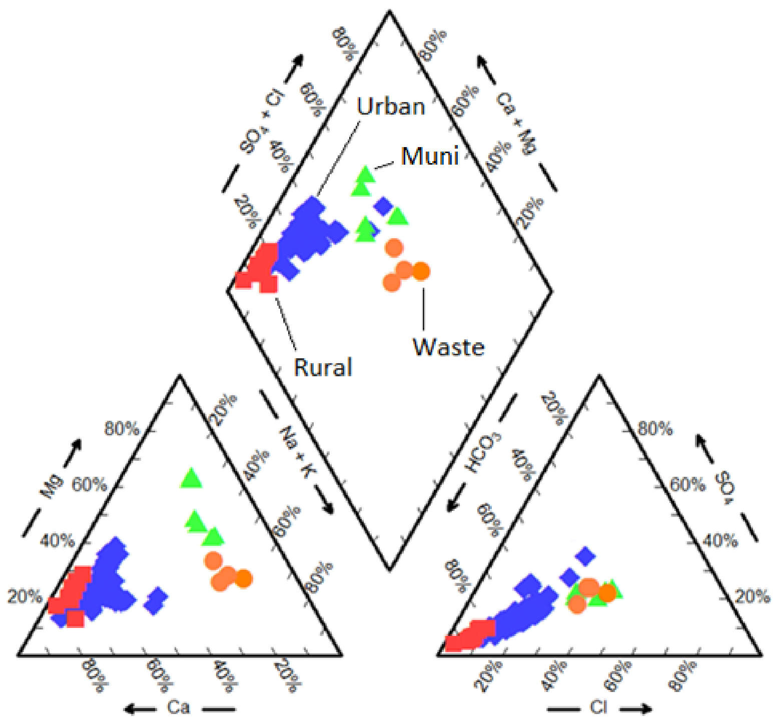


Figure 9: Stiff diagrams for representative samples from a rural spring/tributary site (Rural), an urban spring/tributary site (Urban), City of Austin municipal water collected in the Bull Creek watershed (Muni), and Austin area wastewater (Waste).

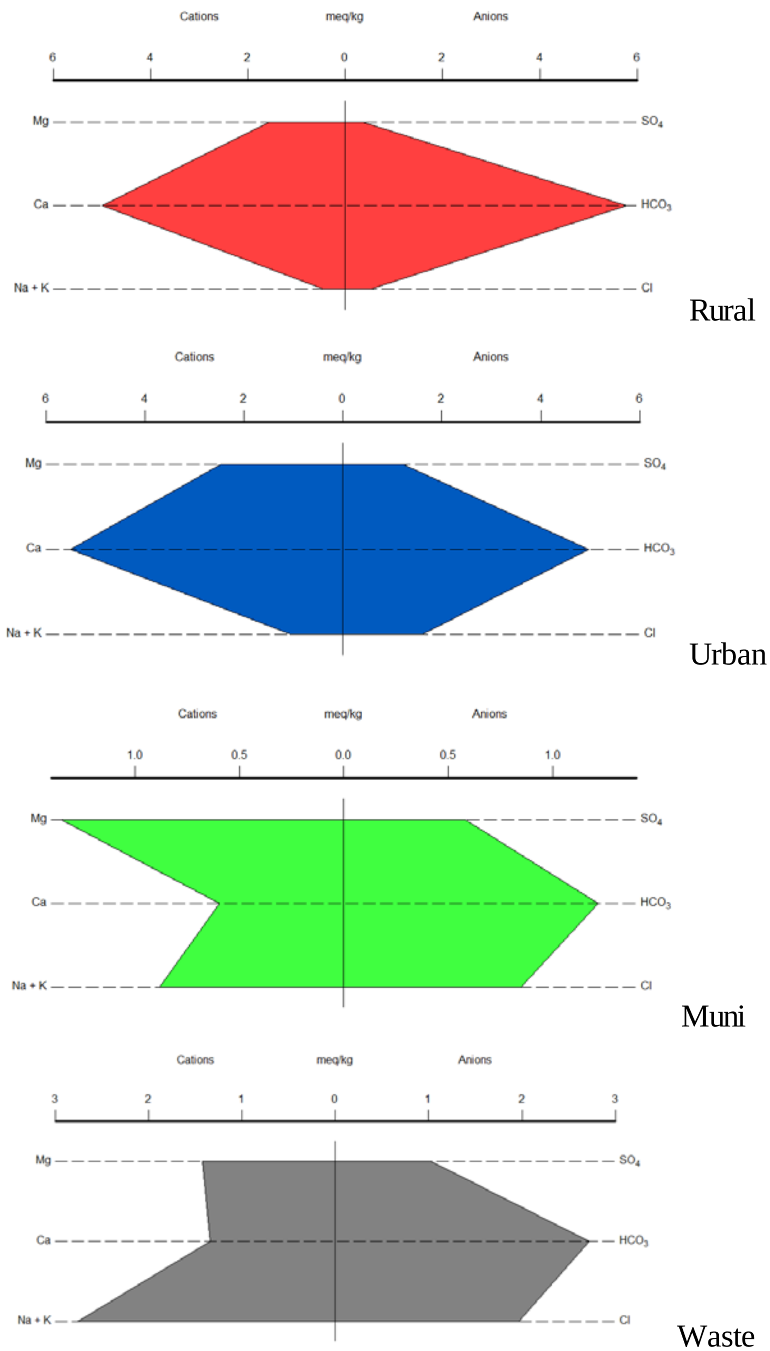


Figure 10: Sodium vs. chloride for Bull Creek springs and tributaries, along with City of Austin municipal water from the Bull Creek watershed and wastewater from the greater Austin area. The black line represents a 1:1 ratio of Na:Cl.

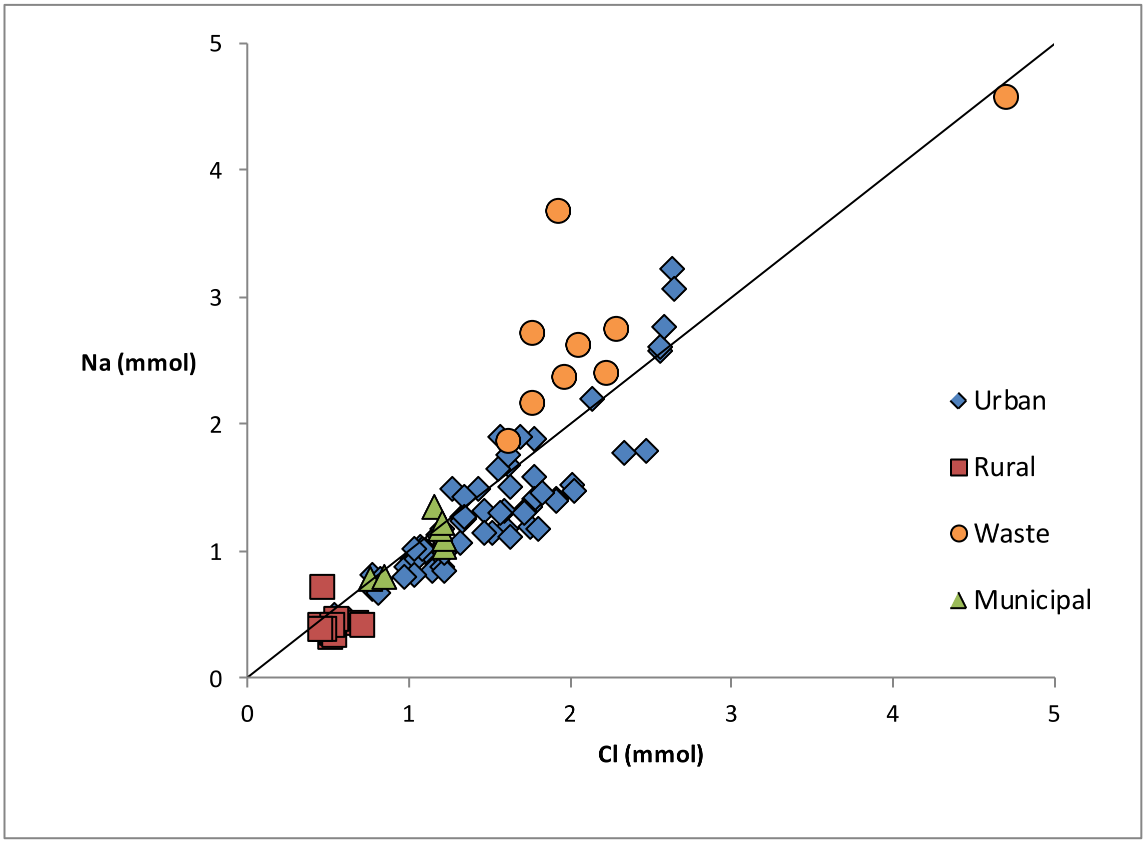
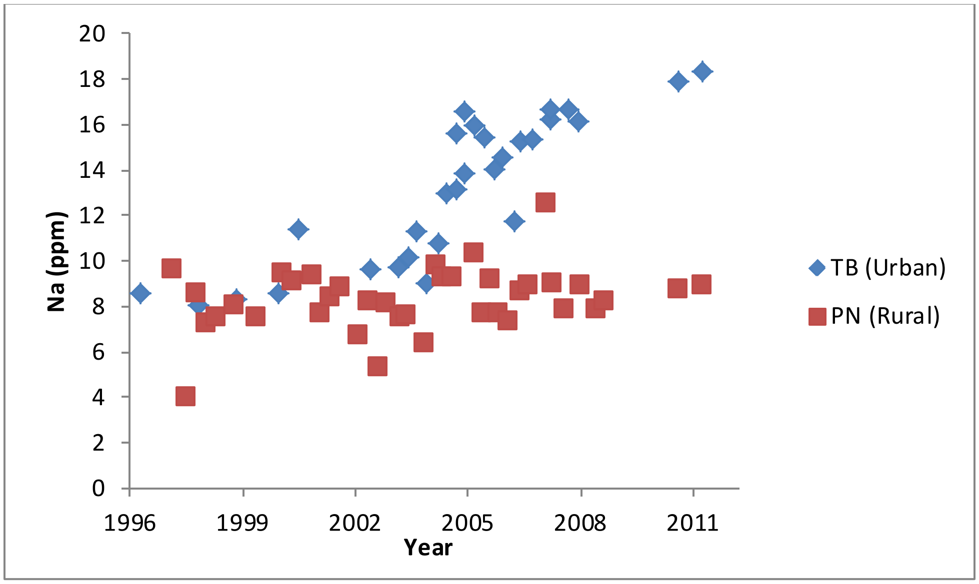


Figure 11: Interannual time series data at selected urban and a rural sites for concentrations of sodium and chloride. (City of Austin, 2014)



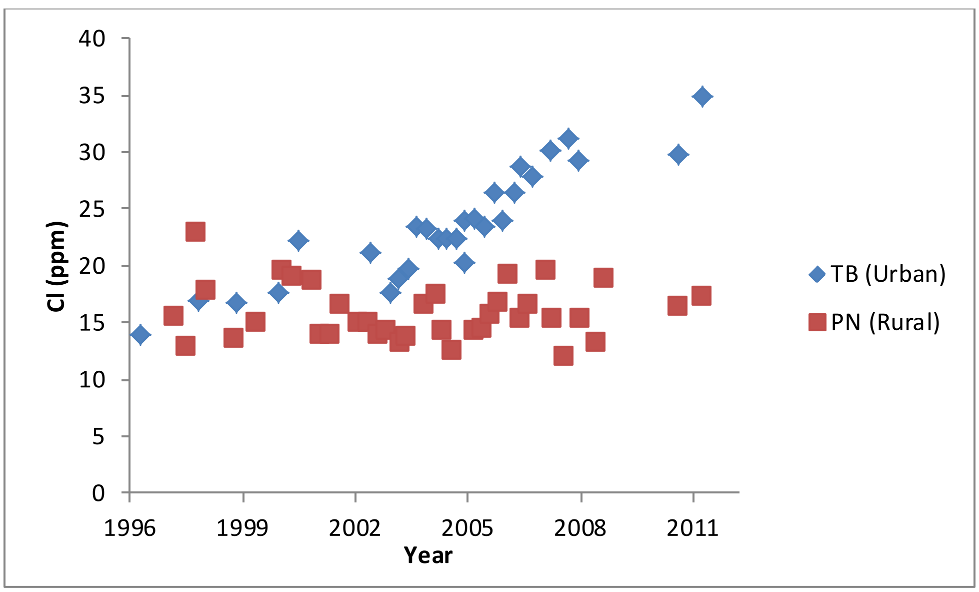


Figure 12: $^{87}Sr/^{86}Sr$ values for samples included in the Bull Creek study. Untreated wastewater data is from the greater Austin area, provided by a City of Austin manhole investigation (City of Austin, 2012). Two of the three irrigated soils were collected from private residences in the Shoal Creek watershed to the east, near its border with the Bull Creek watershed. All other samples are from the Bull Creek watershed.

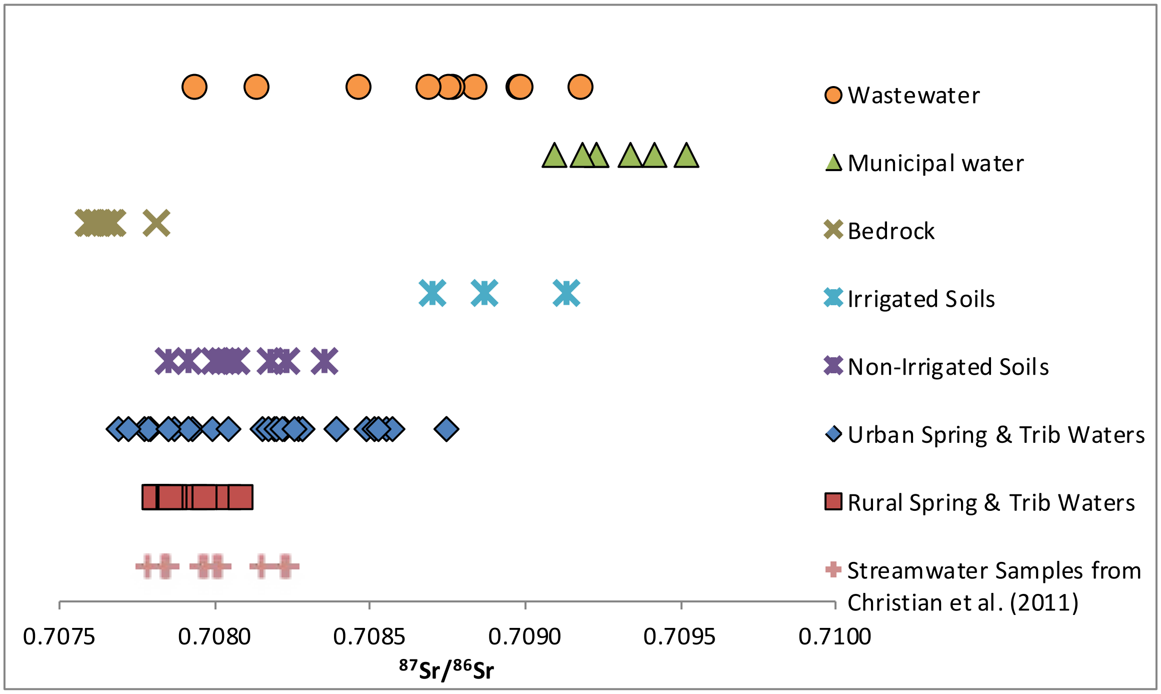


Figure 13: $^{87}Sr/^{86}Sr$ vs. 1/Sr for Bull Creek springs and tributaries, along with City of Austin municipal water from the Bull Creek watershed and wastewater from the greater Austin area. The blue line represents a mixing line between a municipal water sample and a rural spring water sample. The percentages along the line indicate the relative contribution of municipal water along the mixing line. The black line indicates the pathway of geochemical evolution for a municipal water sample dissolving limestone with $^{87}Sr/^{86}Sr = 0.70765$.

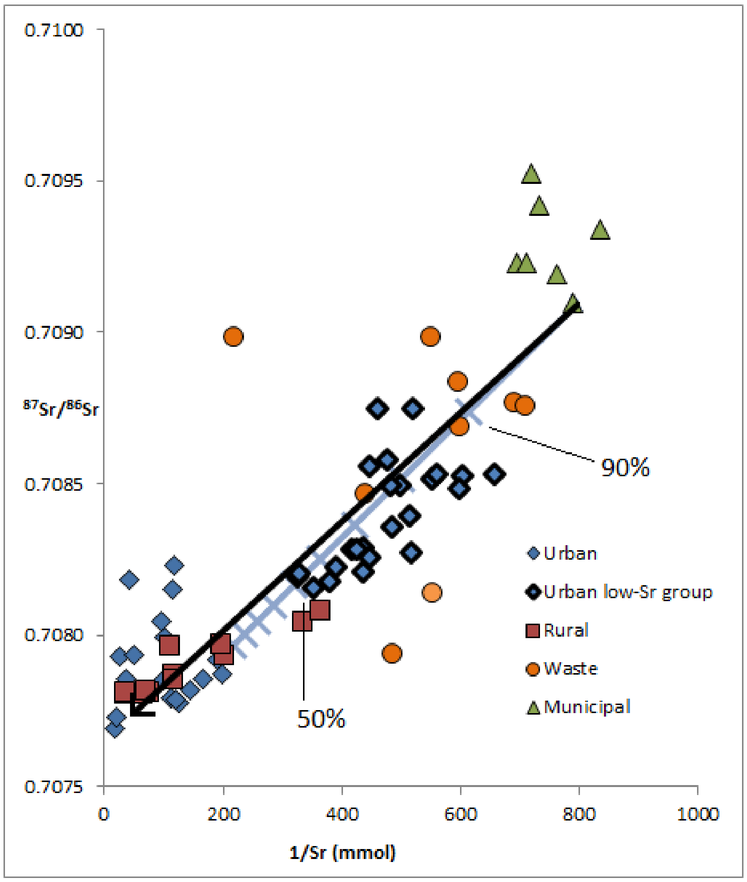


Figure 14: $^{87}Sr/^{86}Sr$ vs. F for Bull Creek springs and tributaries, along with City of Austin municipal water from the Bull Creek watershed and wastewater from the greater Austin area.

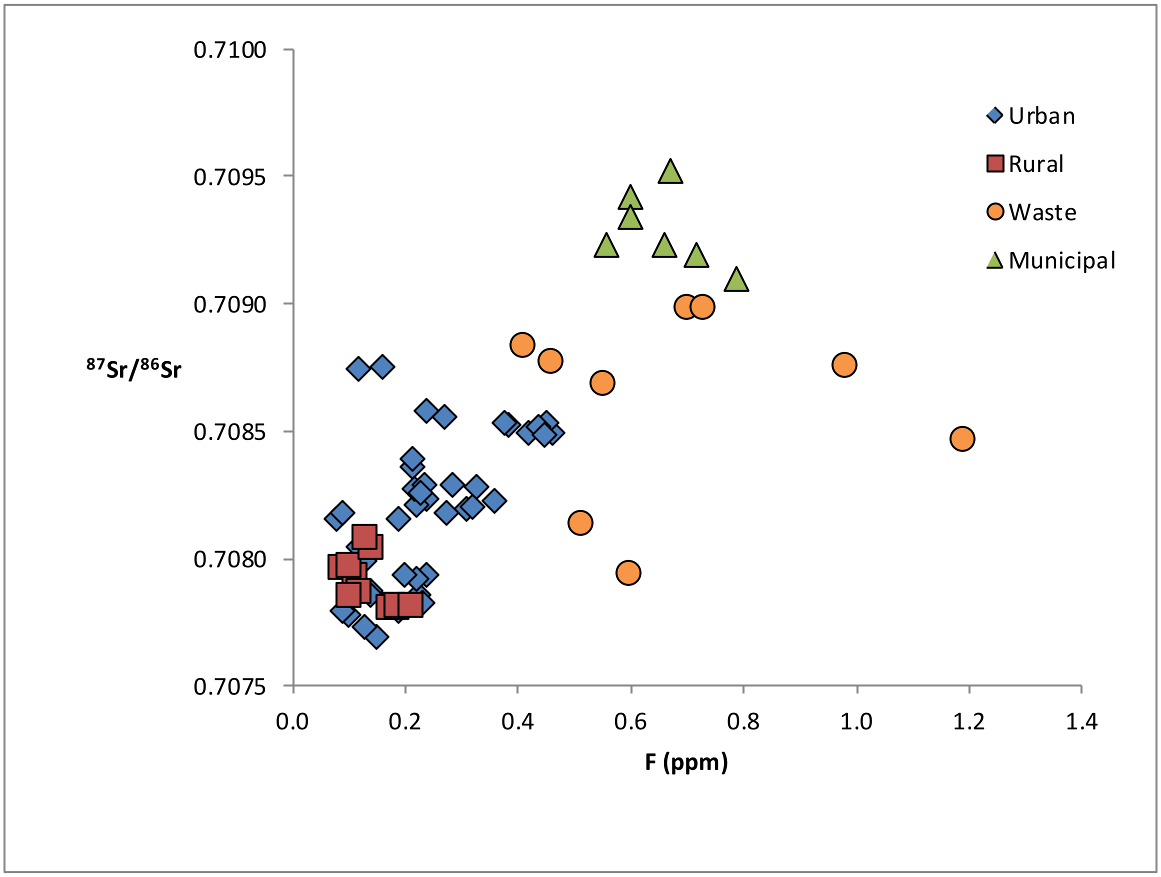


Figure 15: Ca vs. Sr for Bull Creek springs and tributaries, along with City of Austin municipal water from the Bull Creek watershed and wastewater from the greater Austin area. The black line illustrates the geochemical evolution of municipal water dissolving limestone with 250 ppm Sr (Sr estimate taken from Musgrove et al. 2004). Symbol sizes approximate the 5% analytical uncertainty associated with ICP-Q-MS measurements.

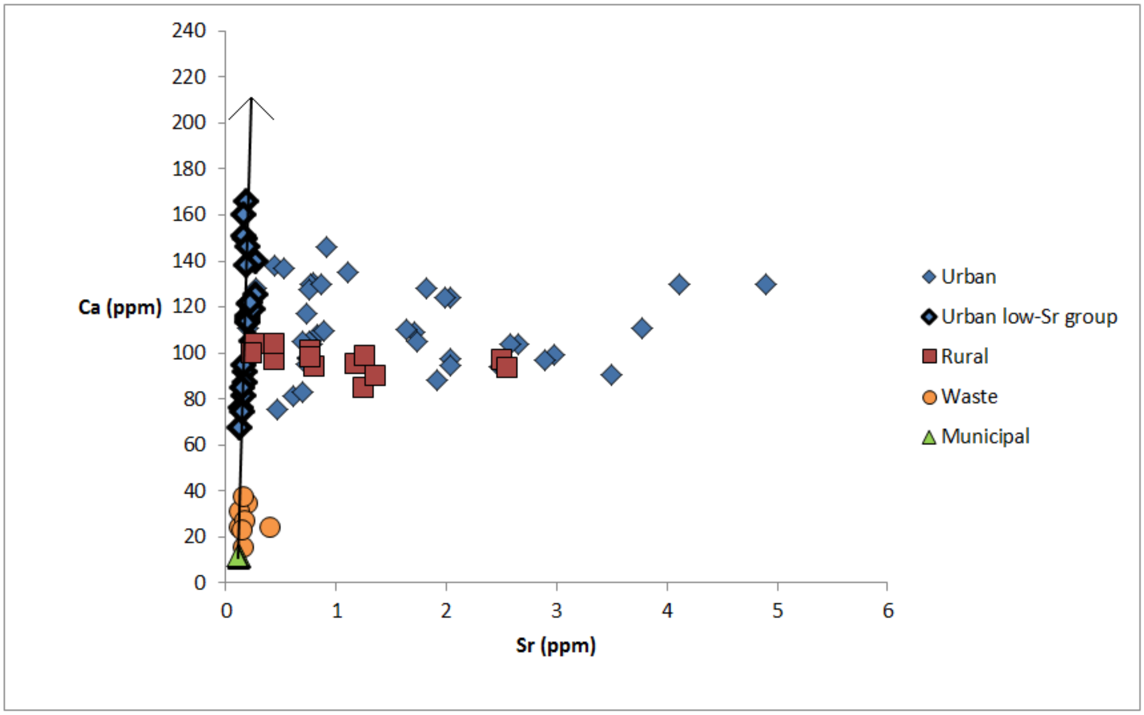


Table 1: Aqueous chemistry and field parameters. 2σ represents the internal reproducibility of the individual analyses.

Site	Classification	Date	T (°C)	pH	Cond (µs/cm)	$^{87}Sr/^{86}Sr$	2σ Internal	Sr (ppm)	Ca	Mg	Na	K	SO_4	Cl	F	HCO_3	NO_3	Charge Balance	$SI_{Calcite}$
AE	Urban Tributary	24-Jul-12	31.1	8.4	664	0.707931	0.000006	3.50	90	23	19	2.7	86	41	0.24	250	<0.5	1.8%	0.890
AE	Urban Tributary	27-Jul-12	32.9	8.0	752	NM	NM	3.77	111	25	19	2.8	89	43	0.26	299	<0.5	2.9%	0.620
AN	Urban Tributary	24-Jul-12	31.7	8.3	928	0.708180	0.000006	2.04	97	21	74	4.0	128	93	0.27	270	2.8	0.6%	0.786
AN	Urban Tributary	27-Jul-12	33.6	7.9	942	NM	NM	1.92	88	24	70	4.1	158	94	0.38	212	<0.5	0.3%	0.240
AS	Urban Tributary	24-Jul-12	27.4	7.4	732	0.707857	0.000006	2.48	94	23	27	1.3	54	62	0.22	286	8.3	0.6%	0.123
AS	Urban Tributary	27-Jul-12	27.8	8.0	751	NM	NM	2.50	94	22	27	1.3	55	64	0.23	281	6.7	0.4%	0.495
AS	Urban Tributary	10-Aug-12	27.1	7.9	804	NM	NM	2.65	104	24	32	1.4	60	68	0.15	283	1.6	4.5%	0.424
AS	Urban Tributary	25-Sep-12	24.4	7.9	797	NM	NM	2.58	104	26	35	1.3	66	72	0.14	293	0.8	3.8%	0.423
AS	Urban Tributary	7-Mar-13	13.6	7.4	764	NM	NM	2.98	99	25	32	1.1	59	63	0.12	292	5.5	3.4%	-0.002
AS	Urban Tributary	21-Jun-13	24.2	7.6	778	NM	NM	2.89	97	23	30	1.3	52	61	0.15	304	<0.5	2.1%	0.170
BF	Urban Tributary	27-Jul-12	27.8	7.2	845	NM	NM	1.71	109	21	36	3.2	81	63	0.23	314	1.0	1.3%	0.044
BF	Urban Tributary	10-Aug-12	27.3	7.4	933	NM	NM	2.04	124	27	43	3.1	76	63	0.15	373	<0.5	4.3%	0.168
BF	Urban Tributary	25-Sep-12	25.6	7.9	899	NM	NM	1.98	124	27	44	3.0	105	56	0.13	327	<0.5	6.3%	0.549
CC	Urban Tributary	24-Jul-12	22.6	7.8	1013	0.708152	0.000006	0.77	130	26	59	3.4	103	91	0.19	376	6.9	1.4%	0.706
CC	Urban Tributary	27-Jul-12	23	7.7	1036	NM	NM	0.76	127	26	60	3.5	107	91	0.22	361	6.3	1.9%	0.374
[1]FB	Urban Tributary	7-Mar-13	18.9	7.3	886	0.708400	0.000006	0.18	149	19	24	2.5	43	38	0.22	443	13.0	3.2%	0.196
FB	Urban Tributary	21-Jun-13	20.8	7.2	897	0.708393	0.000006	0.17	151	18	22	1.7	44	36	0.21	448	12.6	2.4%	0.106
FE	Urban Tributary	24-Jul-12	24.9	7.9	732	0.708282	0.000006	0.21	121	18	21	2.6	47	42	0.33	358	4.5	2.5%	0.602
FE	Urban Tributary	27-Jul-12	25.3	7.8	747	0.708286	0.000006	0.20	116	17	20	2.5	46	43	0.29	343	3.9	1.6%	0.517
FE	Urban Tributary	10-Aug-12	27.3	7.7	764	0.708285	0.000006	0.21	113	18	24	2.5	45	47	0.23	321	2.4	4.4%	0.358
FE	Urban Tributary	23-Aug-12	24.1	7.6	694	NM	NM	0.20	111	17	20	2.4	42	35	0.24	334	1.1	3.4%	0.251
FE	Urban Tributary	25-Sep-12	23.6	7.9	708	0.708259	0.000006	0.20	114	17	22	2.5	43	37	0.23	335	1.3	4.2%	0.592
[1]FE	Urban Tributary	7-Mar-13	13.1	7.9	723	0.708251	0.000006	0.20	115	19	23	2.4	42	42	0.22	326	1.9	5.8%	0.570
FE	Urban Tributary	21-Jun-13	24.5	7.9	625	0.708270	0.000007	0.17	94	16	16	2.3	31	28	0.22	328	<0.5	-0.4%	0.508

Table 1 (cont.)

Site	Classification	Date	T (^{o}C)	pH	Cond (μs/cm)	^{87}Sr/^{86}Sr	2σ Internal	Sr (ppm)	Ca	Mg	Na	K	SO_4	Cl	F	HCO_3	NO_3	Charge Balance	$SI_{Calcite}$
[1]FG	Urban Tributary	7-Mar-13	15	8.0	653	0.707864	0.000006	0.61	81	26	23	2.7	51	40	0.23	285	<0.5	2.8%	0.426
FG	Urban Tributary	21-Jun-13	24.6	8.2	593	0.707920	0.000006	0.46	75	21	18	2.6	27	28	0.22	281	<0.5	3.6%	0.652
FN	Urban Tributary	24-Jul-12	26.2	8.1	674	0.708494	0.000006	0.18	92	20	26	3.2	44	54	0.42	295	4.0	0.2%	0.681
FN	Urban Tributary	27-Jul-12	26.2	8.2	682	0.708494	0.000006	0.18	87	20	26	3.1	42	52	0.46	277	2.2	1.6%	0.645
FN	Urban Tributary	10-Aug-12	29.2	8.1	692	0.708518	0.000006	0.16	81	19	28	3.4	37	47	0.44	281	0.8	1.1%	0.575
FN	Urban Tributary	23-Aug-12	23.8	8.0	613	0.708530	0.000006	0.16	85	18	26	3.2	33	42	0.38	274	1.1	3.9%	0.465
FN	Urban Tributary	25-Sep-12	25.8	8.4	527	0.708484	0.000006	0.15	74	18	27	3.3	32	43	0.45	245	<0.5	4.1%	0.757
[1]FN	Urban Tributary	7-Mar-13	15.4	8.2	574	0.708578	0.000006	0.13	67	19	29	3.1	38	47	0.45	258	<0.5	-0.8%	0.567
FN	Urban Tributary	21-Jun-13	25	8.1	597	0.708524	0.000008	0.15	76	17	23	3.4	29	39	0.39	264	<0.5	2.0%	0.529
FW	Urban Tributary	24-Jul-12	26.1	7.4	860	0.708192	0.000005	0.27	125	24	31	3.1	59	62	0.31	376	9.7	1.8%	0.161
FW	Urban Tributary	27-Jul-12	25.1	7.3	906	NM	NM	0.28	128	25	32	3.1	62	68	0.28	384	5.5	1.7%	0.087
MV	Urban Tributary	24-Jul-12	24.2	7.8	702	0.708229	0.000006	0.74	98	19	29	3.4	43	48	0.24	311	5.8	2.3%	0.357
MV	Urban Tributary	27-Jul-12	24.2	7.4	734	NM	NM	0.75	98	20	30	3.3	45	52	0.24	315	2.8	1.7%	0.013
MV	Urban Tributary	10-Aug-12	26.6	7.9	791	NM	NM	0.83	108	21	34	3.4	45	51	0.19	354	<0.5	2.8%	0.577
MV	Urban Tributary	25-Sep-12	24.2	8.1	740	NM	NM	0.78	104	21	33	3.2	43	48	0.21	314	<0.5	6.2%	0.704
MV	Urban Tributary	7-Mar-13	17.4	8.0	738	NM	NM	0.70	83	20	38	2.5	48	57	0.18	291	<0.5	0.7%	0.440
MV	Urban Tributary	21-Jun-13	22.7	7.6	724	NM	NM	0.73	95	20	34	3.1	32	45	0.20	342	<0.5	2.5%	0.219
PC	Urban Tributary	7-Mar-13	14.7	7.9	767	NM	NM	0.75	105	22	38	1.4	58	55	0.10	324	0.5	3.7%	0.544
PC	Urban Tributary	21-Jun-13	25.5	7.9	854	0.707852	0.000006	0.89	110	22	43	1.9	70	60	0.11	333	<0.5	3.2%	0.549
TR	Urban Tributary	24-Jul-12	22.4	7.6	835	0.707792	0.000005	0.79	130	21	27	1.9	55	57	0.19	377	16.6	1.3%	0.588
TR	Urban Tributary	27-Jul-12	23.5	7.6	875	NM	NM	1.11	135	21	26	1.8	57	58	0.21	369	12.1	2.9%	0.366
TR	Urban Tributary	10-Aug-12	29.8	8.1	800	NM	NM	1.64	110	23	30	1.5	59	57	0.15	303	0.9	5.7%	0.716
TR	Urban Tributary	25-Sep-12	26	8.0	840	NM	NM	1.82	128	24	29	1.9	55	48	0.14	324	3.9	10.3%	0.744

Table 1 (cont.)

Site	Classification	Date	T (^oC)	pH	Cond (µs/cm)	$^{87}Sr/^{86}Sr$	2σ Internal	Sr (ppm)	Ca	Mg	Na	K	SO_4	Cl	F	HCO_3	NO_3	Charge Balance	$SI_{Calcite}$
BW	Urban Spring	29-Aug-10	22.71	7.3	895	0.707689	0.000005	4.90	130	25	33	1.8	61	65	0.15	364	5.1	4.6%	0.011
BW	Urban Spring	12-Apr-11	NM	7.2	895	0.707726	0.000006	4.11	130	23	34	1.4	67	72	0.13	360	7.7	2.4%	-0.054
FY	Urban Spring	29-Aug-10	19.79	6.9	632	0.708154	0.000005	0.25	119	12	12	0.9	17	19	0.08	354	7.5	4.2%	-0.395
FY	Urban Spring	15-Apr-11	NM	6.9	611	0.708175	0.000006	0.23	105	11	11	1.0	18	23	0.09	325	6.6	1.3%	-0.447
SH	Urban Spring	24-Aug-10	NM	7.4	1050	0.708748	0.000006	0.19	166	24	41	1.6	71	88	0.16	407	28.7	4.1%	0.274
SH	Urban Spring	12-Apr-11	NM	7.5	1056	0.708746	0.000005	0.17	160	22	41	1.3	71	83	0.12	399	28.7	3.3%	0.363
TB	Urban Spring	29-Aug-10	20.36	6.8	854	0.707873	0.000006	0.44	138	26	18	1.0	27	30	0.14	481	11.0	1.9%	-0.291
TB	Urban Spring	12-Apr-11	NM	6.8	854	0.707854	0.000010	0.53	137	29	18	1.0	30	35	0.14	456	9.3	4.3%	-0.328
TF	Urban Spring	24-Aug-10	22.9	7.3	682	0.707778	0.000006	0.70	105	16	19	0.7	23	37	0.10	348	2.0	0.8%	-0.038
TF	Urban Spring	12-Apr-11	NM	6.9	687	0.707789	0.000008	0.73	117	16	15	0.4	20	29	0.09	373	1.8	3.0%	-0.356
TL	Urban Spring	28-Aug-10	22.14	6.8	777	0.708202	0.000006	0.27	140	21	23	2.7	37	37	0.32	405	5.2	6.8%	-0.355
TL	Urban Spring	22-Apr-11	NM	6.9	753	0.708223	0.000006	0.23	122	19	23	4.4	42	43	0.36	344	7.0	5.5%	-0.384
TS	Urban Spring	24-Aug-10	23.64	7.1	1000	0.707992	0.000006	0.87	130	24	50	2.6	79	76	0.13	398	1.6	2.0%	-0.129
TS	Urban Spring	12-Apr-11	NM	7.4	1074	0.708047	0.000010	0.91	146	28	64	2.5	105	92	0.12	368	2.2	6.7%	0.184
TT	Urban Spring	28-Aug-10	21.09	7.1	777	0.707932	0.000006	1.73	105	22	40	2.2	62	58	0.20	299	0.3	6.0%	-0.270
TT	Urban Spring	12-Apr-11	NM	7.8	760	NM	NM	2.03	94	22	35	2.4	64	58	0.22	315	0.1	-0.4%	0.401
TW	Urban Spring	19-Aug-10	NM	7.0	989	0.708557	0.000006	0.20	146	32	30	1.8	59	61	0.27	468	12.1	1.9%	-0.115
TW	Urban Spring	12-Apr-11	NM	7.3	885	0.708578	0.000008	0.18	138	33	30	1.6	54	56	0.24	428	7.6	5.2%	0.138
ED	Rural Tributary	24-Jul-12	25.8	8.1	586	0.707808	0.000005	2.50	97	26	10	1.2	32	24	0.19	353	2.5	1.5%	0.761
ED	Rural Tributary	27-Jul-12	26	8.1	652	0.707813	0.000005	2.56	94	25	10	1.2	31	26	0.21	336	3.5	1.5%	0.668
EM	Rural Tributary	24-Jul-12	25.8	7.4	632	0.707812	0.000006	1.18	95	19	7	0.9	19	18	0.18	347	2.4	0.1%	0.055
EM	Rural Tributary	27-Jul-12	24.4	7.4	646	0.707819	0.000005	1.26	98	23	8	0.9	20	19	0.19	359	1.7	1.9%	0.089
EN	Rural Tributary	24-Jul-12	26.7	8.0	547	0.707814	0.000006	1.25	85	19	8	1.3	25	18	0.18	312	<0.5	0.0%	0.567
EN	Rural Tributary	27-Jul-12	26.4	7.7	580	0.707806	0.000006	1.36	90	20	8	1.3	27	19	0.17	308	0.8	2.9%	0.283

Table 1 (cont.)

Site	Classification	Date	T (^{o}C)	pH	Cond (μs/cm)	$^{87}Sr/^{86}Sr$	2σ Internal	Sr (ppm)	Ca	Mg	Na	K	SO_4	Cl	F	HCO_3	NO_3	Charge Balance	$SI_{Calcite}$
[1]PN	Rural Tributary	7-Mar-13	17.2	7.6	547	0.707842	0.000006	0.75	90	16	9	0.5	18	16	0.10	312	<0.5	2.1%	0.129
PN	Rural Tributary	21-Jun-13	20.4	7.8	588	0.707965	0.000006	0.80	94	17	9	0.5	18	17	0.09	322	<0.5	2.9%	0.409
FK	Rural Spring	23-Aug-10	21.62	7.3	594	0.707871	0.000006	0.77	101	17	9	0.6	15	16	0.12	344	<0.1	3.3%	-0.032
FK	Rural Spring	12-Apr-11	NM	7.2	571	0.707856	0.000008	0.77	98	16	9	0.5	18	17	0.10	321	<0.1	4.0%	-0.180
LN	Rural Spring	24-Aug-10	21.66	7.3	591	0.707934	0.000005	0.44	97	16	9	0.5	17	17	0.11	339	<0.1	1.1%	-0.102
LN	Rural Spring	12-Apr-11	NM	7.0	597	0.707971	0.000008	0.45	104	17	11	0.6	21	20	0.10	339	<0.1	3.5%	-0.338
LR	Rural Spring	28-Aug-10	22.17	7.2	637	0.708045	0.000006	0.26	104	20	9	0.7	15	16	0.14	356	0.8	4.4%	-0.139
LR	Rural Spring	12-Apr-11	NM	7.1	608	0.708084	0.000008	0.24	100	19	10	0.8	17	19	0.13	353	1.8	2.2%	-0.238
[1]CLB	CoA Municipal	21-Jun-13	34.6	9.4	343	0.709461	0.000006	0.12	11	16	27	4.7	31	43	0.60	66	<0.5	3.6%	0.456
SBK	CoA Municipal	25-Jul-12	21.5	9.3	301	0.709190	0.000006	0.11	11	15	25	3.9	32	43	0.72	60	0.8	0.5%	0.253
SBK	CoA Municipal	27-Jul-12	29.4	9.4	321	0.709230	0.000006	0.13	11	14	24	4.2	30	44	0.66	60	2.0	-1.1%	0.437
SBK	CoA Municipal	10-Aug-12	31.1	9.2	328	0.709230	0.000006	0.12	12	18	31	4.9	30	41	0.56	64	0.5	10.7%	0.259
SBK	CoA Municipal	25-Sep-12	29.1	9.4	333	0.709522	0.000006	0.12	11	18	28	4.4	29	43	0.67	76	0.8	3.8%	0.478
TCB	CoA Municipal	28-Aug-10	NM	9.4	242	0.709096	0.000005	0.11	11	15	18	3.2	22	27	0.79	68	1.1	3.9%	0.503
TCB	CoA Municipal	15-Apr-11	NM	9.3	262	0.709340	0.000006	0.11	12	16	18	3.6	28	30	0.60	74	0.6	2.5%	0.393
4138	CoA Wastewater	NA	NA	NA	NA	0.708757	0.000006	0.12	31	18	62	14	41	63	0.98	156	0.4	7.4%	NA
4139	CoA Wastewater	NA	NA	NA	NA	0.708467	0.000008	0.20	34	17	85	12	120	68	1.19	135	2.1	2.6%	NA
4914	CoA Wastewater	NA	NA	NA	NA	0.708984	0.000008	0.16	15	16	50	20	44	63	0.70	94	0.2	5.2%	NA
4915	CoA Wastewater	NA	NA	NA	NA	0.707938	0.000008	0.18	27	17	54	16	49	70	0.60	166	0.3	-2.0%	NA
4917	CoA Wastewater	NA	NA	NA	NA	0.708987	0.000008	0.40	24	20	60	14	67	73	0.73	149	0.3	-1.2%	NA
4918	CoA Wastewater	NA	NA	NA	NA	0.708840	0.000008	0.15	25	16	63	18	38	81	0.41	165	<0.1	-0.3%	NA
4920	CoA Wastewater	NA	NA	NA	NA	0.708138	0.000008	0.16	37	21	55	NM	50	79	0.51	141	<0.1	3.4%	NA
4921	CoA Wastewater	NA	NA	NA	NA	0.708690	0.000002	0.15	23	20	43	14	52	57	0.55	113	0.2	4.8%	NA
4922	CoA Wastewater	NA	NA	NA	NA	0.708770	0.000002	0.13	24	16	105	26	32	167	0.46	130	0.1	1.1%	NA

CoA = City of Austin   NA = not available   NM = not measured

[1]Measurement of $^{87}Sr/^{86}Sr$ was made after Faraday cup reconfiguration in September 2013

Table 2: $^{87}Sr/^{86}Sr$ for rocks and soils

Bedrock				
Site	Classification	$^{87}Sr/^{86}Sr$	2σ	Notes
FP1	Edwards	0.707623	0.000006	
FP2	Walnut	0.707674	0.000006	
FP3	Glen Rose	0.707597	0.000006	
FP4	Comanche Peak	0.707666	0.000006	
GHT1	Walnut	0.707604	0.000006	
GHT2	Edwards	0.707646	0.000005	
GHT2-NPT	Edwards	0.707685	0.000006	No $NH_4C_2H_3O_2$ pre-treatment prior to leaching
GHT3	Edwards	0.707625	0.000007	
SE1	Glen Rose	0.707817	0.000007	
SE2	Glen Rose	0.707769	0.000005	
SE2-WR	Glen Rose	0.707747	0.000005	Weathered rind included with sample
Soil				
Site	Classification	$^{87}Sr/^{86}Sr$	2σ	Notes
LPS1	Brackett	0.708002	0.000006	
LPS2	Brackett	0.707920	0.000006	
LPS3	Tarrant	0.708185	0.000006	
LPS4	Tarrant-Speck	0.708049	0.000006	Speck Classified as Redland by Snatic
LPS5	Tarrant-Speck	0.708235	0.000006	Close to parking lot, Speck classified as redland by Snatic
SES1	Tarrant	0.707851	0.000006	St Eds Western cliff edge
SES1-W	Tarrant	0.707847	0.000006	Leach performed with H_2O instead of $NH_4C_2H_3O_2$
SES2	Volente	0.708069	0.000006	St Eds scrubland bend trails area
TRS1	Volente	0.708073	0.000006	Talleyran Park volente
TWB	Brackett	0.708030	0.000006	Collected by D. Reyes in urban park
TWT	Tarrant	0.708353	0.000006	Collected by D. Reyes in urban park
WFH	Tarrant	0.708701	0.000006	Collected by D. Reyes in next to Fire Station, irrigated
XB	Tarrant	0.709134	0.000018	Private residence outside of Bull Creek watershed, irrigated
XS	Tarrant	0.708873	0.000006	Private residence outside of Bull Creek watershed, irrigated

GPS coordinates are presented in Table 7.

Table 3: Mean concentration (ppm) ± one standard deviation of various dissolved ions in urban tributary and spring water samples, rural tributary and spring samples, municipal water samples, and untreated wastewater samples. Untreated wastewater data is from the greater Austin area, provided by a City of Austin manhole investigation (personal communication). All other samples were collected from within the Bull Creek watershed.

	Rural (n=14)	Urban (n=65)	Municipal (n=7)	Waste (n=9)
Sr	1.0 ± 0.7	1.1 ± 1	0.12 ± 0.01	0.2 ± 0.1
Ca	96 ± 9	112 ± 22	11 ± 1	27 ± 7
Mg	19 ± 3	21 ± 4	16 ± 2	18 ± 2.1
Na	9 ± 1	31 ± 13	24 ± 5	64 ± 19
K	0.8 ± 0.3	2.4 ± 0.9	4.1 ± 0.6	17 ± 4
SO_4	21 ± 6	56 ± 26	29 ± 3	55 ± 27
Cl	19 ± 3	54 ± 18	39 ± 7	80 ± 34
F	0.14 ± 0.04	0.22 ± 0.1	0.66 ± 0.1	0.7 ± 0.3
HCO_3	336 ± 18	336 ± 57	67 ± 6	139 ± 24
NO_3	1.0 ± 1	4.5 ± 6	0.8 ± 0.6	0.4 ± 0.6

Table 4: Median concentration and range for the various sample types included in the Bull Creek study.

	Rural (n=14)	Urban (n=65)	Municipal (n=7)	Waste (n=9)
Sr	0.78 (0.24-2.6)	0.73 (0.13-4.9)	0.11 (0.11-0.13)	0.16 (0.12-0.40)
Ca	97 (85-104)	110 (67-166)	11 (11-12)	25 (15-37)
Mg	19 (16-26)	21 (11-33)	16 (14-18)	17 (16-21)
Na	9 (7-11)	29 (11-74)	25 (18-31)	60 (43-105)
K	0.7 (0.5-1.3)	2.5 (0.4-4.4)	4.2 (3.2-4.9)	15 (12-26)
SO_4	19 (15-32)	52 (17-158)	30 (22-32)	49 (32-120)
Cl	18 (16-26)	52 (19-94)	43 (27-44)	70 (57-167)
F	0.14 (0.09-0.21)	0.22 (0.08-0.46)	0.66 (0.56-0.79)	0.60 (0.41-1.2)
HCO_3	339 (308-359)	327 (212-481)	66 (60-76)	141 (94-166)
NO_3	0.4 (<0.1-3.5)	2.2 (0.1-29)	0.81 (<0.5-2.0)	0.19 (<0.5-2.05)

Table 5: Mean $^{87}Sr/^{86}Sr$ ± standard deviation for sample types defined in the study. Springs and tributaries were sampled from 2010-2013. Samples from Christian et al. (2011) were collected from Bull Creek in 2002. Two of the three irrigated soil samples were collected from private residences in the Shoal Creek watershed to the east (*Fig. 2*), near its border with the Bull Creek watershed. Untreated wastewater data is from the greater Austin area, provided by a City of Austin manhole investigation. All other samples were collected from within the Bull Creek watershed.

Sample Type	$^{87}Sr/^{86}Sr$
Rural Springs and Tributaries (n=13)	0.70788 ± 0.00010
Urban Springs and Tributaries (n=41)	0.70818 ± 0.00029
Municipal Water (n=7)	0.70928 ± 0.00014
Wastewater (n=9)	0.70861 ± 0.00037
Limestone Bedrock (n=9)	0.70767 ± 0.00008
Non-irrigated soil (n=11)	0.70806 ± 0.00016
Irrigated Soil (n=3)	0.70890 ± 0.00022
Bull Creek streamwater from 2002 (n=8) (Christian, et al., 2011)	0.70803 ± 0.00016

Table 6: Median $^{87}Sr/^{86}Sr$ and range for the various sample types included in the Bull Creek study.

Sample Type	$^{87}Sr/^{86}Sr$
Rural Springs and Tributaries (n=13)	0.70784 (0.70780-0.70808)
Urban Springs and Tributaries (n=41)	0.70820 (0.70769-0.70875)
Municipal Water (n=7)	0.70923 (0.70910-0.70952)
Wastewater (n=9)	0.70876 (0.70794-0.70899)
Limestone Bedrock (n=9)	0.70765 (0.70760-0.70782)
Non-irrigated soil (n=11)	0.70805 (0.70785-0.70835)
Irrigated Soil (n=3)	0.70887 (0.70870-0.70913)
Bull Creek Main Trunk (n=8) (Christian, et al., 2011)	0.70801 (0.70784-0.70824)

Table 7: GPS coordinates for samples from the Bull Creek watershed.

	Site	Latitude	Longitude		Site	Latitude	Longitude
Tributaries	AE	30.38267	-97.76894	Soil	WFH	30.43256	-97.77884
	AN	30.3829	-97.76935		LPS1	30.37963	-97.78422
	AS	30.38245	-97.7689		LPS2	30.38643	-97.78519
	BF	30.39194	-97.77421		LPS3	30.38908	-97.78845
	CC	30.42657	-97.8141		LPS4	30.37894	-97.77833
	ED	30.40426	-97.79301		LPS5	30.37799	-97.77991
	EM	30.4604	-97.79385		SES1	30.40425	-97.79077
	EN	30.41618	-97.79561		SES2	30.40585	-97.79090
	FE	30.40804	-97.75447		TPS1	30.42214	-97.79858
	FG	30.40636	-97.75383		TWB	30.43113	-97.78073
	FN	30.4105	-97.75639		TWT	30.43246	-97.77961
	FW	30.41082	-97.75726		XB	30.37112	-97.74872
	MV	30.42323	-97.79353		XS	30.36651	-97.74741
	PC	30.42177	-97.80903	Bedrock	FP1	30.41114	-97.75504
	PN	30.41931	-97.81087		FP2	30.40926	-97.75505
	TR	30.42078	-97.79829		FP3	30.40706	-97.75394
Springs	BW	30.37296	-97.76912		FP4	30.40691	-97.75111
	FK	30.41901	-97.81270		GHT1	30.38839	-97.75838
	FY	30.42988	-97.83481		GHT2	30.38866	-97.75963
	LN	30.41364	-97.82246		GHT3	30.3884	-97.75927
	LR	30.40464	-97.82644		LP1	30.37891	-97.78172
	SH	30.37284	-97.76428		SE1	30.40425	-97.79077
	TB	30.43154	-97.81687		SE2	30.40433	-97.78964
	TF	30.42695	-97.81846	Municipal water	CLB	30.35712	-97.78564
	TL	30.40959	-97.75256		SBK	30.45321	-97.82700
	TS	30.42541	-97.81465		TCB	30.40452	-97.85131
	TT	30.39728	-97.76981				
	TW	30.43098	-97.78225				

Table 8: Bedrock and soil by individual sub-watershed.

Site Name	Area (m^2)	kGr m^2	kW m^2	kEd m^2	kCp m^2	kGr%	kW%	kEd%	kCp%	Total	Brackett m^2	Speck & San Saba m^2	Tarrant m^2	Volente m^2	Br%	SS%	Ta%	Vo%	Total
BW	487,405	7,178	57,671	422,320	0	*0*	*0*	*1*	*0*	1	236,235	0	251,114	0	*0*	*0*	*1*	*0*	1
FY	669,297	0	1,196	667,737	0	*0*	*0*	*1*	*0*	1	0	0	669,204	0	*0*	*0*	*1*	*0*	1
FK	901,594	161,619	261,583	477,960	0	*0*	*0*	*1*	*0*	100%	85,257	0	703,349	112,868	*0*	*0*	*1*	*0*	100%
LN	4,187,022	230,902	658,196	3,295,814	0	*0*	*0*	*1*	*0*	100%	116,154	0	3,720,839	330,826	*0*	*0*	*1*	*0*	100%
LR	2,087,942	0	159,543	1,927,285	0	*0*	*0*	*1*	*0*	100%	19,181	27,055	1,927,900	90,026	*0*	*0*	*1*	*0*	99%
SH	143,304	0	10,879	132,295	0	*0*	*0*	*1*	*0*	100%	37,487	0	105,800	0	*0*	*0*	*1*	*0*	100%
TW	447,803	0	0	406,242	41,307	*0*	*0*	*1*	*0*	100%	42,093	0	341,629	0	*0*	*0*	*1*	*0*	86%
TT	2,569,458	209,062	397,997	1,771,471	189,763	*0*	*0*	*1*	*0*	100%	1,272,685	74,792	1,103,922	102,110	*0*	*0*	*0*	*0*	99%
TF	2,473,671	44,312	352,092	2,000,617	75,434	*0*	*0*	*1*	*0*	100%	100,680	0	2,227,059	145,589	*0*	*0*	*1*	*0*	100%
TS	4,838,923	107,141	261,897	3,918,406	548,915	*0*	*0*	*1*	*0*	100%	534,737	130,446	3,757,347	283,887	*0*	*0*	*1*	*0*	97%
TL	522,931	0	0	474,325	46,074	*0*	*0*	*1*	*0*	100%	102,846	57,209	362,808	0	*0*	*0*	*1*	*0*	100%
TB	46,521	0	0	45,246	1,253	*0*	*0*	*1*	*0*	100%	2,108	0	44,407	0	*0*	*0*	*1*	*0*	100%
AE	2,919,600	365,768	435,703	2,021,296	68,879	*0*	*0*	*1*	*0*	99%	1,604,743	0	1,110,852	176,981	*1*	*0*	*0*	*0*	99%
AN	7,465,500	784,729	666,973	5,331,900	625,993	*0*	*0*	*1*	*0*	99%	3,709,237	337,501	2,805,871	554,138	*0*	*0*	*0*	*0*	99%
AS	1,456,200	241,815	283,902	916,579	0	*0*	*0*	*1*	*0*	99%	740,563	0	691,966	10,246	*1*	*0*	*0*	*0*	99%
BF	2,965,500	424,004	482,848	1,869,374	187,931	*0*	*0*	*1*	*0*	100%	1,562,318	80,690	1,201,075	109,026	*1*	*0*	*0*	*0*	100%
CC	4,858,200	90,349	238,710	3,919,102	560,599	*0*	*0*	*1*	*0*	99%	537,308	120,136	3,751,595	256,114	*0*	*0*	*1*	*0*	96%
ED	99,000	18,689	48,130	32,134	0	*0*	*0*	*0*	*0*	100%	0	0	98,987	0	*0*	*0*	*1*	*0*	100%
EM	1,240,200	156,858	240,250	825,047	0	*0*	*0*	*1*	*0*	99%	0	0	1,211,042	11,530	*0*	*0*	*1*	*0*	99%
EN	1,696,500	160,458	319,146	1,212,790	0	*0*	*0*	*1*	*0*	100%	0	0	1,555,599	137,373	*0*	*0*	*1*	*0*	100%
FB	302,400	0	3,111	255,427	41,991	*0*	*0*	*1*	*0*	99%	171,893	0	128,249	478	*1*	*0*	*0*	*0*	99%
FE	547,200	0	441	488,542	45,648	*0*	*0*	*1*	*0*	98%	123,522	38,534	372,741	0	*0*	*0*	*1*	*0*	98%
FG	558,000	198	12,117	470,157	58,198	*0*	*0*	*1*	*0*	97%	162,992	85,101	292,350	396	*0*	*0*	*1*	*0*	97%
FN	1,746,900	0	16,045	1,546,639	162,081	*0*	*0*	*1*	*0*	99%	670,164	213,865	708,987	127,198	*0*	*0*	*0*	*0*	98%
FW	818,100	0	32,884	658,480	126,369	*0*	*0*	*1*	*0*	100%	513,406	0	270,183	33,804	*1*	*0*	*0*	*0*	100%
MV	5,607,000	169,160	252,158	4,605,491	532,450	*0*	*0*	*1*	*0*	99%	607,435	398,263	4,073,667	154,177	*0*	*0*	*1*	*0*	93%
PC	9,081,000	341,619	839,346	7,139,321	683,157	*0*	*0*	*1*	*0*	99%	808,120	120,136	7,371,239	561,789	*0*	*0*	*1*	*0*	98%
PN	7,398,900	397,411	1,088,436	5,840,226	0	*0*	*0*	*1*	*0*	99%	220,592	27,943	6,493,281	537,579	*0*	*0*	*1*	*0*	98%
TR	1,019,700	82,250	126,353	663,677	146,943	*0*	*0*	*1*	*0*	100%	233,582	0	745,421	40,557	*0*	*0*	*1*	*0*	100%
BC watershed	63,223,309	12,555,661	9,069,977	38,482,529	2,384,148	*0*	*0*	*1*	*0*	99%	19,555,634	1,091,653	36,435,338	5,404,713	*0*	*0*	*1*	*0*	99%

Table 9: Indices of urbanization by individual sub-watershed.

Site	Site Type	TotalArea (m^2)[a]	Real Property Area (m^2)	Road Length (m)	Road Density (m^{-1})[b]	Road Density (ft^{-1})[b]	Impervious Cover Area (m^2)[c]	Impervious Cover %[d]	Adjusted Impervious Cover %[e]	Classification[f]	Median Structure Age
BW	Spring	487,405	407,497	4,721	0	0	48,883	10%	23%	Urban	1978
FK	Spring	901,594	901,592	0	0	0	44,289	5%	5%	Rural	1980
FY	Spring	669,297	609,704	2,469	0	0	311,135	46%	54%	Urban	2001
LN	Spring	4,187,022	4,050,910	7,763	0	0	418,177	10%	13%	Rural	1992
LR	Spring	2,087,942	2,003,468	2,844	0	0	463,442	22%	25%	Rural	1977
SH	Spring	143,304	143,234	0	0	0	44,165	31%	31%	Urban	1971
TB	Spring	46,521	34,480	829	0	0	4,201	9%	30%	Urban	2003
TF	Spring	2,473,671	2,320,999	9,265	0	0	285,769	12%	16%	Urban	1992
TL	Spring	522,931	474,299	1,862	0	0	287,768	55%	62%	Urban	1993
TS	Spring	4,838,923	4,212,190	36,095	0	0	535,080	11%	21%	Urban	1982
TT	Spring	2,569,458	2,247,029	18,032	0	0	282,002	11%	21%	Urban	1990
TW	Spring	447,803	383,614	3,971	0	0	128,873	29%	40%	Urban	1975
AE	Tributary	2,919,600	2,287,097	25,306	0	0	777,725	27%	44%	Urban	n.c.
AN	Tributary	7,465,500	6,460,480	51,477	0	0	1,661,320	22%	33%	Urban	n.c.
AS	Tributary	1,456,200	1,315,150	7,529	0	0	295,064	20%	28%	Urban	n.c.
BF	Tributary	2,965,500	2,588,186	21,511	0	0	283,872	10%	20%	Urban	n.c.
CC	Tributary	4,858,200	4,176,337	36,804	0	0	534,873	11%	22%	Urban	n.c.
ED	Tributary	99,000	98,987	0	0	0	912	1%	1%	Rural	n.c.
EM	Tributary	1,240,200	1,222,573	0	0	0	11,236	1%	2%	Rural	n.c.
EN	Tributary	1,696,500	1,692,972	0	0	0	17,935	1%	1%	Rural	n.c.
FB	Tributary	302,400	262,911	2,161	0	0	88,196	29%	40%	Urban	n.c.
FE	Tributary	547,200	488,579	1,833	0	0	294,876	54%	62%	Urban	n.c.
FG	Tributary	558,000	456,171	3,902	0	0	247,763	44%	59%	Urban	n.c.
FN	Tributary	1,746,900	1,399,170	18,871	0	0	172,666	10%	26%	Urban	n.c.
FW	Tributary	818,100	697,260	7,148	0	0	80,426	10%	22%	Urban	n.c.
MV	Tributary	5,607,000	4,746,233	48,656	0	0	825,297	15%	27%	Urban	n.c.
PC	Tributary	9,081,000	8,077,546	52,865	0	0	1,185,162	13%	22%	Urban	n.c.
PN	Tributary	7,398,900	7,089,934	11,039	0	0	946,091	13%	16%	Rural	n.c.
TR	Tributary	1,019,700	887,260	7,844	0	0	96,473	9%	20%	Urban	n.c.
BK	Whole Watershed	63,223,309	57,231,362	310,665	0	0	8,384,310	13%	21%	Urban	n.c.

[a]Tributary watersheds delineated using a 30 meter cell size

[b]Road length divided by total area

[c]Estimated using impervious cover approximations for various land use types

[d]Impervious cover area divided by real property area

[e]Includes roads as 80% impervious cover - Impervious cover area plus 80% of the difference between total area and real property area, divided by total area

[f]Road density less than 1×10^{-2} ft^{-1} and adjusted impervious cover less than 30%

n.c. - not calculated

Table 10: Mean ion concentration and $^{87}Sr/^{86}Sr$ for springs and tributaries.

Site	$^{87}Sr/^{86}Sr$	Sr (ppm)	Ca	Mg	Na	K	SO_4	Cl	F	HCO_3	NO_3	# $^{87}Sr/^{86}Sr$ samples	# ion analysis samples
BW	0.707708	4.51	130	24	34	1.6	64	69	0.14	362	6.4	2	2
FY	0.708165	0.24	112	11	11	1.0	18	21	0.09	339	7.0	2	2
FK	0.707863	0.77	100	17	9	0.6	16	17	0.11	332	0.0	2	2
LN	0.707952	0.44	100	16	10	0.5	19	18	0.11	339	0.0	2	2
LR	0.708065	0.25	102	20	10	0.7	16	18	0.14	354	1.3	2	2
SH	0.708747	0.18	163	23	41	1.5	71	86	0.14	403	28.7	2	2
TW	0.708567	0.19	142	32	30	1.7	57	58	0.26	448	9.9	2	2
TT	0.707932	1.88	100	22	37	2.3	63	58	0.21	307	0.2	1	2
TF	0.707783	0.71	111	16	17	0.6	22	33	0.10	361	1.9	2	2
TS	0.708019	0.89	138	26	57	2.6	92	84	0.13	383	1.9	2	2
TL	0.708213	0.25	131	20	23	3.5	39	40	0.34	375	6.1	2	2
TB	0.707864	0.48	138	18	28	1.0	28	32	0.14	468	10.2	2	2
AE	0.707931	3.63	101	24	19	2.8	87	42	0.25	275	0.1	1	2
AN	0.708180	1.98	93	22	72	4.0	143	94	0.33	241	1.6	1	2
AS	0.707857	2.68	99	24	31	1.3	57	65	0.17	290	3.8	1	6
BF	NM	1.91	119	25	41	3.1	87	61	0.17	338	0.3	0	3
CC	0.708152	0.76	129	26	60	3.4	105	91	0.20	368	6.6	1	2
ED	0.707810	2.53	95	25	10	1.2	32	25	0.20	345	3.0	2	2
EM	0.707815	1.22	97	21	8	0.9	19	19	0.18	353	2.1	2	2
EN	0.707810	1.30	87	20	8	1.3	26	18	0.18	310	0.5	2	2
FB	0.708374	0.18	150	18	23	2.1	44	37	0.21	445	12.8	2	2
FE	0.708265	0.20	112	18	21	2.5	42	39	0.25	335	2.1	6	7
FG	0.707870	0.53	78	24	21	2.6	39	34	0.23	283	0.2	2	2
FN	0.708516	0.16	80	19	26	3.2	36	46	0.43	271	1.2	6	7
FW	0.708192	0.27	127	25	32	3.1	61	65	0.29	380	7.6	1	2
MV	0.708229	0.75	98	20	33	3.1	43	50	0.21	321	1.4	1	6
PC	0.707852	0.82	107	22	41	1.6	64	58	0.11	328	0.5	1	2
PN	0.707881	0.77	92	16	9	0.5	18	16	0.09	317	0.0	2	2
TR	0.707792	0.79	130	22	28	1.9	55	57	0.19	377	16.6	1	4

NM = not measured

Table 11: Physical and chemical correlations for bedrock units, soil units and measures of urbanization for the individual subwatersheds, and average water composition for each corresponding spring and tributary site in the Bull Creek watershed. IC% = impervious cover; Adj IC% = adjusted impervious cover; kGr = Glen Rose formation; kW = Walnut formation; kEd = Edwards formation; kCp = Comanche Peak formation; Br = Brackett soil; SS = Speck and San Saba Clay soil; Ta = Tarrant soil; Vo = Volente soil.

r^2	$^{87}Sr/^{86}Sr$	Sr	Ca	Mg	Na	K	SO_4	Cl	F	HCO_3	NO_3
Road Index	0.08	0.00	0.09	0.31	0.19	0.27	0.16	0.21	0.24	0.05	0.01
IC%	0.00	0.03	0.00	0.07	0.00	0.01	0.01	0.01	0.01	0.00	0.00
Adj IC%	0.01	0.02	0.00	0.01	0.00	0.01	0.00	0.00	0.01	0.00	0.00
kGr	0.25	0.31	0.17	0.02	0.02	0.02	0.01	0.02	0.01	0.18	0.11
kW	0.30	0.25	0.14	0.00	0.10	0.16	0.02	0.07	0.08	0.07	0.07
kEd	0.24	0.23	0.14	0.05	0.01	0.01	0.01	0.01	0.00	0.12	0.09
kCp	0.11	0.12	0.08	0.12	0.26	0.51	0.18	0.23	0.29	0.03	0.02
Br	0.04	0.16	0.01	0.09	0.17	0.32	0.31	0.25	0.24	0.05	0.01
SS	0.06	0.06	0.11	0.00	0.02	0.35	0.00	0.00	0.37	0.15	0.06
Ta	0.06	0.10	0.00	0.11	0.21	0.47	0.33	0.26	0.36	0.10	0.00
Vo	0.05	0.00	0.17	0.05	0.00	0.00	0.00	0.01	0.01	0.19	0.21
$^{87}Sr/^{86}Sr$		0.26	0.18	0.02	0.08	0.16	0.05	0.12	0.22	0.06	0.25
Sr			0.04	0.10	0.02	0.00	0.13	0.04	0.00	0.14	0.06
Ca				0.07	0.11	0.00	0.06	0.20	0.02	0.70	0.62
Mg					0.25	0.17	0.35	0.38	0.09	0.02	0.02
Na						0.44	0.82	0.88	0.07	0.00	0.03
K							0.50	0.39	0.59	0.06	0.00
SO_4								0.79	0.10	0.03	0.01
Cl									0.08	0.00	0.13
F										0.06	0.00
HCO_3											0.38

Table 12: Results for NBS SRM-987 for Sr isotope measurements. 2σ = internal reproducicility of individual analyses.

Analysis Date	$^{87}Sr/^{86}Sr$	2σ
23-Sep-10	0.710248	0.000005
23-Sep-10	0.710239	0.000005
3-Feb-11	0.710248	0.000006
3-Feb-11	0.710256	0.000006
3-Feb-11	0.710265	0.000006
26-Aug-11	0.710266	0.000008
14-Oct-11	0.710265	0.000008
14-Oct-11	0.710270	0.000008
3-Apr-12	0.710262	0.000006
3-Apr-12	0.710271	0.000006
30-Nov-12	0.710263	0.000006
30-Nov-12	0.710277	0.000006
17-Jul-13	0.710273	0.000006
25-Jul-13	0.710263	0.000007
25-Jul-13	0.710266	0.000007
27-Jul-13	0.710277	0.000006
27-Jul-13	0.710273	0.000006
13-Aug-13	0.710270	0.000005
13-Aug-13	0.710259	0.000006
16-Aug-13	0.710268	0.000006
16-Aug-13	0.710271	0.000007
20-Dec-13	0.710214	0.000006
21-Dec-13	0.710227	0.000006
21-Dec-13	0.710220	0.000005

Table 13: TIMS QA/QC – Results for analytical replicates of Sr isotope samples. 2σ = internal reproducility of individual analyses.

Site	Sampling Date	Type	$^{87}Sr/^{86}Sr$	2σ
[1]FN	27-Jul-12	Tributary	0.708498	0.000006
[1]FE	10-Aug-12	Tributary	0.708273	0.000005
FN	23-Aug-12	Tributary	0.708568	0.000006
[1]FN	23-Aug-12	Tributary	0.708516	0.000006
[1]FN	25-Sep-12	Tributary	0.708528	0.000005
GHT2	13-Feb-13	Bedrock	0.707665	0.000006
SES1	13-Feb-13	Soil	0.707845	0.000007

[1]Measurement of $^{87}Sr/^{86}Sr$ was made after Faraday cup reconfiguration in September 2013

Table 14: TIMS QA/QC - Chemistry blanks for Sr isotope samples. 2σ = internal reproducility of individual analyses.

Date	Sr (pg)
30-Nov-12	32
25-Jul-13	9
13-Aug-13	<1
16-Aug-13	6
20-Dec-13	1

Table 15: TIMS QA/QC - Filtered replicates for Sr isotope samples. 2σ = internal reproducility of individual analyses.

Site	Sampling Date	$^{87}Sr/^{86}Sr$	2σ
TW	19-Aug-10	0.7085572	0.000008
AH	24-Aug-10	0.708746	0.000005

Table 16: ICP-Q-MS QA/QC - NIST 1643e measurements

NIST 1643e										
Actual	0.0334	3.33	0.828	2.14	0.210	Agreement				
Analysis Date	Sr (ppm)	Ca	Mg	Na	K	Sr	Ca	Mg	Na	K
6-Aug-12	0.0331	3.33	0.860	2.16	0.208	99%	100%	104%	101%	99%
6-Aug-12	0.0333	3.36	0.824	2.09	0.213	100%	101%	100%	98%	101%
6-Aug-12	0.0332	3.21	0.809	2.07	0.210	99%	97%	98%	97%	100%
6-Aug-12	0.0335	3.33	0.786	2.05	0.218	100%	100%	95%	96%	104%
6-Aug-12	0.0340	3.36	0.812	2.05	0.208	102%	101%	98%	96%	99%
13-Jun-13	0.0318	3.21	0.845	2.23	0.221	95%	97%	102%	104%	106%
13-Jun-13	0.0324	3.22	0.810	2.13	0.209	97%	97%	98%	100%	100%
13-Jun-13	0.0330	3.29	0.807	2.12	0.210	99%	99%	97%	99%	100%
14-Jun-13	0.0329	3.19	0.835	2.20	0.212	99%	96%	101%	103%	101%
14-Jun-13	0.0329	3.20	0.828	2.20	0.210	98%	96%	100%	103%	100%
14-Jun-13	0.0329	3.21	0.803	2.13	0.206	98%	96%	97%	100%	98%
14-Jun-13	0.0329	3.22	0.822	2.17	0.211	99%	97%	99%	102%	101%
14-Jun-13	0.0333	3.24	0.802	2.15	0.213	100%	97%	97%	101%	102%
14-Jun-13	0.0328	3.21	0.810	2.15	0.213	98%	96%	98%	101%	102%
29-Jun-13	0.0331	3.34	0.835	2.21	0.218	99%	100%	101%	103%	104%
29-Jun-13	0.0331	3.33	0.849	2.22	0.219	99%	100%	102%	104%	104%
29-Jun-13	0.0323	3.30	0.825	2.18	0.216	97%	99%	100%	102%	103%

Table 17: ICP-Q-MS QA/QC - Analytical replicates.

							Agreement				
Replicated Sample	Collection Date	Sr (ppm)	Ca	Mg	Na	K	Sr	Ca	Mg	Na	K
FN	10-Aug-12	0.16	81.5	18.3	27.6	3.3	100%	101%	98%	98%	96%
FE	23-Aug-12	0.20	113	17.6	20.6	2.5	101%	102%	102%	102%	102%
FE	23-Aug-12	0.20	111	17.9	21.0	2.5	101%	100%	104%	104%	102%
FB	7-Mar-13	0.18	151	18.5	23.6	2.5	99%	101%	99%	100%	101%
PC	21-Jun-13	0.75	111	21.4	42.8	1.9	84%	102%	99%	98%	98%

Table 18: ICP-Q-MS QA/QC - Spike Recoveries.

Spiked Sample	Collection Date	Sr	Ca	Mg	Na	K
CC	24-Jul-12	96%	88%	83%	87%	96%
EN	24-Jul-12	100%	165%	88%	92%	91%
FN	10-Aug-12	99%	95%	99%	97%	95%
FE	23-Aug-12	99%	99%	95%	96%	96%
FB	7-Mar-13	98%	101%	95%	98%	96%
PC	21-Jun-13	100%	97%	96%	95%	94%

Table 19: HPLC QA/QC - Alltech anion mix 3 measurements

	Actual	20	20	20	Agreement		
Injection Volume %	Analysis Date	Cl (ppm)	SO_4	NO_3	Cl	SO_4	NO_3
100%	25-Jun-13	18.6	18.5	18.5	93%	93%	92%
25%	26-Jun-13	4.9	5.1	4.9	98%	102%	99%
100%	26-Jun-13	18.3	18.2	18.6	92%	91%	93%
50%	26-Jun-13	9.8	10.1	9.6	98%	101%	96%
100%	1-Jul-13	18.8	19.1	18.4	94%	95%	92%
100%	2-Jul-13	19.1	19.9	18.5	95%	100%	93%
100%	2-Jul-13	19.1	20.0	18.2	96%	100%	91%

Table 20: HPLC QA/QC - Alltech anion mix 8 measurements

	Actual	50	100	Agreement	
Injection Volume %	Analysis Date	Cl (ppm)	SO_4	Cl	SO_4
100%	25-Jun-13	47.7	99.5	95%	100%
25%	26-Jun-13	12.9	25.4	103%	102%
100%	26-Jun-13	47.0	101	94%	101%
50%	26-Jun-13	24.6	50.2	98%	100%
100%	1-Jul-13	47.7	102	95%	102%
100%	1-Jul-13	48.7	106	97%	106%
100%	2-Jul-13	48.7	104	97%	104%

Table 21: HPLC QA/QC - Analytical Replicates

Replicated Sample	Collection Date	Cl (ppm)	SO_4	NO_3	Cl	SO_4	NO_3
FN	10-Aug-12	46.4	36.6	0.6	98%	99%	75%
FE	23-Aug-12	34.3	40.3	1.2	98%	96%	110%
FB	25-Sep-12	33.1	32.0	3.8	100%	99%	99%
FB	7-Mar-13	39.0	43.5	13.8	102%	100%	106%
PN	21-Jun-13	16.8	17.9	BDL	101%	101%	BDL

BDL = below detection limit

Table 22: FISE QA/QC - 1 ppm standard measurements

Analysis Date	F (ppm)
1-Aug-12	0.95
1-Aug-12	0.93
1-Aug-12	0.93
1-Aug-12	0.9
12-Sep-13	1.03
12-Sep-13	1.06
12-Sep-13	1.03
12-Sep-13	1.01
12-Sep-13	1.00
12-Sep-13	1.07

Table 23: FISE QA/QC - Analytical Replicates

Replicated Sample	Collection Date	F (ppm)	Agreement
FE	10-Aug-12	0.25	105%
FE	23-Aug-13	0.24	102%
MV	29-Sep-13	0.21	99%
FE	7-Mar-13	0.23	105%
FN	21-Jun-13	0.38	99%

Table 24: Water sampling QA/QC - Field blanks

	TIMS	ICPMS					HPLC			ISE	Titration
Collection Date	Sr (pg)	Sr (ppm)	Ca	Mg	Na	K	Cl	SO_4	NO_3	F	HCO_3
24-Jul-12	16	BDL	BDL	BDL	BDL	BDL	3.7	BDL	1.1	BDL	NM
27-Jul-12	138	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.9	BDL	NM
10-Aug-12	121	BDL	0.35	BDL	0.16	0.13	BDL	BDL	BDL	BDL	1
23-Aug-12	21	BDL	0.33	BDL	0.09	0.07	BDL	BDL	BDL	BDL	1
25-Sep-12	22	BDL	0.08	BDL	BDL	0.03	BDL	BDL	BDL	BDL	1
7-Mar-13	5529	0.004	4.8	0.05	BDL	BDL	0.5	BDL	BDL	BDL	18
21-Jun-13	5	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	1

Table 25: UT Laboratory QA/QC – Detection Limits

ICP-Q-MS					HPLC			FISE
Sr (ppm)	Ca	Mg	Na	K	SO_4	Cl	NO_3	F
0.001	0.059	0.013	0.068	0.018	1	2	0.5	0.003

Appendix A: 1947 Aerial Mosaic of the Upper Bull Creek Watershed (Marquez, 1947)

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